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Physical, Chemical, and Biological Treatment Techniques for Industrial Wastes. Volume I

Arthur D. Little, Inc., Cambridge, Mass.

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PHYSICAL, CHEMICAL, AND BIOLOGICAL TREATMENT TECHNIQUES FOR INDUSTRIAL WASTES

Volume I

This final report (SW-148c.1) describes work performed
for the Federal solid waste management program
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Volumes I and II examine 47 unit engineering processes for their applicability to the task of treating hazardous industrial wastes.

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There is a strong need for treatment processes which can detoxify, destroy, or apply resource recovery principles to industrial wastes. This study examined 47 unit engineering processes for their applicability to the task of treating hazardous industrial wastes. Some of these unit processes are commonly used for industrial waste treatment while others require further R&D efforts before they will become commercially attractive. Four (dialysis, electrophoresis, freeze drying and zone refining) were found not to be applicable to waste treatment. Part Two of this report presents comprehensive descriptions of each of the unit processes, including information on the basic principles, areas of application, economics, energy and environmental considerations, and an outlook for future use on industrial wastes. Thus, Part Two is in essence an up-to-date reference textbook on potential treatment processes.

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FOREWORD

There is a strong need for treatment processes which can detoxify, destroy, or apply resource recovery principles to industrial wastes. This study examined 47 unit engineering processes for their applicability to the task of treating hazardous industrial wastes.

Of these unit processes, 10 can be applied for phase separation, 3 are basically for pre-processing of bulk solids or tars, 12 react chemically to destroy or detoxify the hazardous components, while 25 can be used to separate specific components within the waste stream. Some of these unit processes are commonly used for industrial waste treatment while others require further R&D efforts before they will become commercially attractive. Four (dialysis, electrophoresis, freeze drying and zone refining) were found not to be applicable to waste treatment.

Part Two of this report presents comprehensive descriptions of each of the unit processes, including information on the basic principles, areas of application, economics, energy and environmental considerations, and an outlook for future use on industrial wastes. Thus, Part Two is in essence an up-to-date reference textbook on potential treatment processes.

A major problem is how to make all of the information in Part Two readily available and useful. Section IV of Part One focuses on that problem, and is organized as a series of reference tables to be used when screening processes for application to an individual waste stream. These tables will provide a method of screening out processes that do not have any potential for the waste in question.

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PREFACE

BASES FOR COST ESTIMATES

All capital cost estimates were prepared on the basis of equipment and construction costs for a time period of early 1976. The bases used were either the Chemical Engineering Plant Cost Index of 188 or a Marshall and Swift Equipment Cost Index of 450. (Reference – Chemical Engineering March 29, 1976) for all of the processes except those based on biological activity. For the biological processes, the cost basis was the Engineering News Record Construction Cost Index (ENR March 18, 1976) of 2300.

Operating labor costs were taken as $12.00/hour which was assumed to include supervision and overhead charges. Annual maintenance (labor and material) was taken as a fraction of investment and was varied according to the estimated severity of the operations. Chemicals were charged at unit prices derived from Chemical Market Reporter. Electricity was charged at $0.02/kwh.

The annualized costs of capital were established on the basis of a 10-year capital recovery factor with money borrowed at 10 percent interest. This method of annualizing capital costs has been widely used in pollution control cost estimating and is equivalent to off-the-books financing that might be obtained through the use of industrial pollution control bonds. The capital recovery factor for these cost estimates is 0.16274, i.e., the annual cost of capital is 16.274 percent of the total capital investment.

If cost estimates are to be prepared for different capacities, the following exponential scaling factors based on capacities are suggested.

Capital Investment	
All processes except biological	0.7
Biological processes	0.5
Operating Labor	0.3
Utilities and chemicals	1.0

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PART ONE

SUMMARY

I. BACKGROUND

A typical manufacturing establishment takes in raw materials, adds value through one or more processing steps, and produces one or more products for sale. It is seldom possible to convert 100% of the raw materials into salable products, so there almost always is some waste or residual. In addition, there are usually gaseous and aqueous emissions, but recent air and water pollution control regulations limit the release of potentially hazardous materials in effluent water and gas streams. Water treatment and air pollution control systems usually act to remove rather than to detoxify hazardous materials. Potentially toxic or hazardous materials removed from air and water streams, or generated as waste in the course of normal industrial production, are not currently subject to Federal regulation; and most frequently these residual waste materials are dumped on land.

Indiscriminate dumping of industrial processing wastes can lead to groundwater contamination, or other adverse effects, often 40 or 50 years after the initial waste disposal. Although methods have been explored to reduce leaching to groundwater, by, for example, encapsulating wastes prior to burial, and/or securing sanitary landfills, the amount of land available for dump sites still is decreasing, while the volume of residuals requiring disposal is increasing.

As a normal course of events, large industrial plants are constantly seeking ways to convert process residuals into profitable by-products that can either be returned to the raw material stream within the plant, or marketed outside. The success of such resource recovery efforts is governed almost entirely by economics. The net costs of recovery (actual treatment costs minus credits for the recovered resource) must be less than the costs of alternative waste management methods. As long as the alternative of land dumping at $2-3/ton remains, the economically allowable investment in waste treatment is severely restrained. Clearly, however, continued release or re-release of contaminants into the environment via leaching to groundwater, surface water run-off, or airborne dusts from land burial sites cannot be permitted. As land disposal costs begin to increase in response to pressures for protecting the environment, other hazardous waste management alternatives can become more attractive.

For the management of industrial processing wastes from the point of generation to the point of ultimate (and environmentally adequate) disposal, three technically desirable alternatives to immediate land burial are:

- resource recovery (materials or energy),
- detoxification, and
- volume reduction, coupled with disposal.

The resource recovery alternative is obviously attractive not only from the point of view of conserving materials supplies now beginning to be recognized as finite, but also as a potential means of reducing the quantity of hazardous material requiring disposal. The detoxification alternative interposes a step prior to disposal that makes the waste stream innocuous, so that lowest-cost disposal methods become applicable. The volume-reduction alternative simply reduces the magnitude of the waste disposal problem, permitting efficient utilization of available secured chemical landfill sites.

II. SCOPE OF THE STUDY

A. OBJECTIVES

The objectives of this study are to identify physical, chemical, and biological treatment methods with potential utility for the design and implementation of resource recovery, detoxification, and/or volume-reduction systems. This study is not meant to provide detailed designs of such systems for specific waste streams; rather, it aims to provide background information that will aid subsequent systems designers in selecting relevant treatment processes.

For each potentially applicable treatment method identified, Part Two of this study addresses, in depth, the:

- Technical characteristics
- Underlying physical, chemical, and/or biological principles,
- Operating characteristics
  - Physical and chemical properties of suitable feed streams
  - Mode of operation
  - Physical and chemical properties of the output streams
- Operating experience
  - Principal current applications (including waste treatment)
  - Potential applications for treatment of hazardous wastes
- Capital and operating costs (including credits for products recovered)
- Environmental impacts
  - Waste streams or residues associated with the treatment process
  - Pollution control or further treatment requirements
- Energy requirements
  - electricity
  - fossil fuels
- Outlook for industrial waste treatment
  - current state-of-the-art
  - factors favoring and inhibiting widespread use
  - development needs

To increase the utility of the information provided on individual treatment processes, Part One of this report presents general guidelines for selecting those treatment processes which are potentially applicable to wastes of particular characteristics.

B. APPROACH

1. Literature Search

An extensive literature search on potentially useful processes was initiated. The Hazardous Waste Management Division (HWMD) of the EPA made information available from its files, and conducted a computerized search of the SWIRS (Solid Waste Information Retrieval System) data bank for pertinent articles. Prior HWMD contractor reports(1,2,3) and the Division's Report to Congress(4) were reviewed. An independent search of the general literature and patent literature was performed and trade and professional organizations and government agencies, industries, and universities were contacted.

By the time of this report, 47 treatment processes had been identified (Table 1). (Incineration and encapsulation processes are excluded, as they are the subjects of other U.S. EPA studies.) At least two processes were assigned to each of 12 ADL technical staff specialists for in-depth investigation, thus the study team was able to develop a high level of technical and professional expertise on all processes of real potential applicability to industrial wastes.

2. Interview Program

The processes identified in the Literature Search were subdivided into the five categories defined in Table 2. These categories were set up to guide the amount of effort required by the contractor for each process. A site visit and personal interview program was planned to obtain first-hand information and expert opinion or advice on the processes in each category.

In addition to hundreds of telephone contacts, each expert made two to seven site visits for each identified Category II-V process. The visits covered commercial and industrial waste treatment facilities, equipment suppliers; industrial laboratories; government laboratories; and/or experts. In all instances, each specialist gathered information for other team members as appropriate.

3. Analysis of Information

a. Mini-Reports

On the basis of the initial Literature Search, each technical specialist prepared a preliminary state-of-the-art report on his/her assigned processes. These reports, generally 5-10 pages in length, were used to help assign processes to categories (Table 2); to identify key information gaps for investigation in the Interview Program; and to report progress to date to EPA.

TABLE 1

TREATMENT PROCESSES IDENTIFIED

Physical

Air Stripping
Suspension Freezing
Carbon Adsorption
Centrifugation
Dialysis
Distillation
Electrodialysis
Electrophoresis
Evaporation
Filtration
Flocculation
Flotation
Freeze Crystallization
Freeze Drying
High Gradient Magnetic Separation
Ion Exchange
Liquid Ion Exchange
Steam Distillation
Resin Adsorption
Reverse Osmosis
Sedimentation
Liquid-Liquid Extracting of Organics
Steam Stripping
Ultrafiltration
Zone Refining

Chemical

Calcination and Sintering
Catalysis
Chlorinolysis
Electrolysis
Hydrolysis
Microwave Discharge
Neutralization
Oxidation
Ozonolysis
Photolysis
Precipitation
Reduction

Biological

Activated Sludge
Aerated Lagoon
Anaerobic Digestion
Composting
Enzyme Treatment
Trickling Filter
Waste Stabilization Pond

Pretreatment of Bulk Solids of Tars

Crushing and Grinding
Cryogenics
Dissolution

TABLE 2

CATEGORIZATION OF PROCESSES BY EFFORT NEEDED

No.	Category Description	Work Effort for Each Process
I.	Process is not applicable in a useful way to wastes of interest to this program	Enough to justify category assignment
II.	Process might work in 5-10 years, but needs research effort first	Same as Category I, plus description of what questions need to be answered by future effort
III.	Process appears useful for hazardous wastes, but needs development work	Same as Category II plus description of current uses and projected applications to industrial wastes
IV.	Process is developed but not commonly used for hazardous wastes	Same as Category III
V.	Process will be common to most industrial waste processors	Description of how used, where, for what, including economics, environment, energy, etc.

b Final Report

After an extensive field Interview Program, each Mini-Report was revised and expanded into comprehensive final treatment process reports (Part Two). The results on individual processes are summarized and compared herein.

III. TREATMENT PROCESSES INVESTIGATED

Most of the 47 processes identified in this study (Table 1) are unit processes or operations, several of which would normally have to be linked in series to form a complete treatment system for a particular waste stream. Four of the processes, however, were found to have little or no potential utility in a hazardous waste management system, that is:

- *Dialysis*, while it does separate high-molecular-weight molecules from low-molecular-weight salts, results in two output streams, both of which are more dilute than the original stream but not suitable for direct disposal.

- *Electrophoresis* could in principle be used to remove suspended colloidal matter (1-20 μ particle size) from any aqueous or organic medium, provided that the colloidal particles were charged relative to the liquid phase. However, the process is not only underdeveloped, but also unpromising. There are no scientific or practical guides upon which to base a development program, so there is some question that high removal efficiencies could be achieved. Suitable equipment is not available. Furthermore, in any working unit, electrode reactions would have to be suppressed, the conductivity of the waste stream might have to be below 300 microhms/cm, turbulent mixing would have to be avoided, and potential problems of membrane plugging would have to be solved.

- *Freeze drying* is an operationally difficult, expensive and energy-intensive dewatering process whose use would not appear to be justified in the treatment of any real waste streams.

- *Zone refining* is a slow, costly, energy-intensive process for purification of solids. It can only be operated in batch, on samples weighing less than 10 kg, which are relatively pure. It is impractical for the complex mixtures which are typical of waste streams.

Thus, of the initial 47, this left 43 as potentially useful processes to be investigated. These processes fall naturally into four classes: (1) phase separation processes, potentially useful in volume reduction or resource recovery; (2) component separation processes, capable of physically segregating particular ionic or molecular species from multicomponent, single-phase waste streams; (3) chemical transformation processes, which promote chemical reactions to detoxify, recover, or reduce the volume of specific components in waste streams; and (4) biological treatment methods, which involve chemical transformations brought about by the action of living organisms.

A. PHASE SEPARATION

Waste streams, such as slurries, sludges and emulsions, which are not single phase, will often require a phase-separation process (Table 3) before detoxification or recovery steps can be implemented. Frequently, phase separation permits a significant volume reduction, particularly if the hazardous component is present to a significant extent in only one of the phases. Furthermore, by concentrating the hazardous portion of the stream, sequential processing steps may be accomplished more readily. Phase-separation processes usually are mechanical, inexpensive and simple, and can be applied to a broad spectrum of wastes and waste components.

Emulsions are generally very difficult to separate. Heating, cooling, change of pH, salting out, centrifugation, API separators, etc., may all be tried, but there is no accurate way to predict what might work. Appropriate methods can only be developed empirically, specific to any given situation.

1. Settlable Slurries

Conceptually, the simplest separation process is *sedimentation*, or gravity settling. The output streams will consist of a sludge and a decantable supernatant liquid. If the components of the sludge are at all soluble, the supernatant liquid generally will be a solution. A closely related process and the phase separation process in most common use is *filtration*. *Centrifugation* is essentially a high gravity sedimentation process whereby centrifugal forces are used to increase the rate of particle settling. *Flotation* is used extensively in ore separation, and in fact is the single most important process that has made it possible to recover value from lower and lower grades of metallic and non-metallic ores. It has not been extensively studied for hazardous waste applications. *High-gradient magnetic separation* is a relatively new process that appears to have potential for separating magnetic and paramagnetic particles from slurries.

2. Colloidal Slurries

The basic concept in all the above processes for settable slurries is to get the solid phases to drop out of the liquid phase, through the use of gravitational, centrifugal magnetic, or hydrostatic forces. Such forces generally do not act on colloidal suspended particles.

The simplest and most commonly used colloidal separation process is flocculation. Ultrafiltration has many industrial applications, including waste treatment, and is expected to have many more within the next five years. Further development effort is required, however, to demonstrate its full potential.

TABLE 3

PHASE SEPARATION PROCESSES

		Type of Waste to Which Process is Applicable			
	Process Category[1]	Settlable Slurries[2]	Colloidal Slurries[2]	Sludges[3]	Any Wastes With a Volatile Liquid Phase
V.	Common in Waste Treatment	Sedimentation Filtration	Flocculation	Filtration	Solar Evaporation
IV.	Developed but not commonly used in Waste Treatment	Centrifugation			Distillation (with solvent recovery) Evaporation
III.	Need further development for Waste Treatment	Flotation High-Gradient Magnetic Separation	Ultrafiltration	Freezing	

1. Described in more detail in Table 2.
2. A slurry is defined as a pumpable solid-liquid mixture. It is settlable if the phases separates on standing, and colloidal if they do not.
3. A sludge is defined as a non-pumpable solid-liquid mixture.

3. Sludges

The major phase separation desired in the handling of sludges is dewatering. Vacuum filtration or press filtration are the processes in most common use. Some research has been done on simple freezing, but the process is not well developed and the work that has been done is not promising.

4. Volatiles

Sludges and slurries (colloidal or separable) in which the liquid phase is volatile may be treated by either evaporation or distillation. Solar evaporation is very commonly used. Engineered evaporation or distillation systems would normally be operated if recovery of the liquid is desired.

B. COMPONENT SEPARATION

The many physical processes which act to segregate ionic or molecular species from multicomponent waste streams (Table 4) do not require chemical reactions to be effective. None are so commonly used as to be classified in Category V, but there has been a great deal of experience with most of them in the water treatment field. The majority of Category IV processes act only on aqueous solutions.

C. CHEMICAL TRANSFORMATION

The relatively few processes which involve chemical reactions (Table 5) are the only processes which we found are potentially capable of detoxifying hazardous components in waste streams (in addition to recovering resources or reducing volume for land disposal). By far the two most common processes are neutralization and precipitation. Since there is usually a pH range where the solubility of heavy metal precipitates is at a minimum, neutralization (interpreted broadly as pH adjustment) and precipitation are in fact often used together.

D. BIOLOGICAL TREATMENT

Biological Treatment methods (Table 6) are only effective in aqueous media, and are only capable of breaking down organic components. The four Category V processes are used essentially in polishing of soluble organics. The feed streams must be low in solids (< 1%), free of oil and grease, and non-toxic to the active microorganisms (e.g., heavy metal content less than 10 ppm). The processes yield a biomass sludge for disposal which contains heavy metals and refractory organics not decomposed by the biologically active species present.

The Category IV processes, anaerobic digestion and composting, are useful for more concentrated waste streams and will tolerate solid contents of 5-7% and 50%, respectively. Composting will decompose oils, greases, and tars, yielding a concentrated metal sludge and a leachate containing partially decomposed organics.

TABLE 4

COMPONENT SEPARATION PROCESSES

		Function of Process			
	Process Category	**Removal of heavy metal and toxic anions from aqueous solutions**	**Removal of organics from aqueous solutions**	**Removal of inorganics from liquids, slurries and sludges**	**Solvent Recovery**
IV.	Developed, but not commonly used in Waste Treatment	Liquid Ion Exchange Electrodialysis Reverse Osmosis Ion Exchange	Ultrafiltration Solvent Extraction Carbon Adsorption Resin Adsorption Steam Stripping Air Stripping		Distillation Steam Distillation
III.	Needs further development for Waste Treatment			Freeze crystallization	
II.	Needs further research	Ion Flotation		High-Gradient Magnetic Separation	

TABLE 5

CHEMICAL TRANSFORMATION PROCESSES

Process Category	Treatable Components and Waste Streams					
	Cyanides, phenolics, sulfides, sulfites, and organics in aqueous solution	**Nitrates, carbonates, sulfates, hydroxides, in sludges, tars, and solids**	**Heavy metals in aqueous solution**	**Organic liquids, sludges, slurries tars and solids**	**Acids and Bases**	**Organic liquids**
V. Common in Waste Treatment			Precipitation		Neutralization	
IV. Developed but not commonly used in Waste Treatment	Oxidation Ozonation UV/Ozonolysis UV/Chlorination	Calcination	Reduction			
III. Requires further development for Waste Treatment			Electrolysis	Hydrolysis		Chlorinolysis
II. Needs further research	Photolysis Catalysis		Precipitate Flotation	Catalysis		Microwave

TABLE 6

BIOLOGICAL TREATMENT METHODS

		Functions of Process	
	Process Category	Decomposition of soluble organics in dilute aqueous streams	Decomposition of hydrocarbons (non-chlorinated)
V.	Commonly in Waste Treatment	Activated sludge Aerated Lagoon Trickling Filter Waste Stabilization Pond	
IV.	Developed but not commonly used in Waste Treatment		Composting Anaerobic Digestion
II.	Needs further research	Enzyme Treatment	

Enzyme treatment has been shown to be effective for phenols and some hydrocarbons, but the waste stream must be of constant composition and free of inorganic contamination.

IV. SELECTION OF TREATMENT PROCESSES FOR GIVEN WASTE STREAMS

A. PHILOSOPHY OF APPROACH

There are a variety of ways to approach the problem of selecting the appropriate process(es) for treatment of a particular waste stream. Individual engineers, chemists, equipment manufacturers, salesmen, environmental managers, plant managers, regulatory authorities, etc., will each have slightly different perspectives on the problem, different data needs, and different ways of manipulating the data to reach a final conclusion. No one approach is "right" for everyone. The sequence of steps that to one individual seems necessary and immutable, may to another seem irrelevant or illogical.

Within the scope of this report we cannot duplicate the thought processes of the many different kinds of individuals who might be involved in the selection of waste treatment alternatives. We also cannot impose our own thinking – no matter how logical it may seem to us – on individuals who approach the problem differently. To resolve this dilemma, we have chosen first to pose some of the questions to which various people might require answers before even beginning to match wastes with treatment processes. Next, we have provided a number of examples of possible steps in process selection for some typical wastes. We leave it to the individual reader to decide what questions he must have answered, and in what sequence, in order to be able to develop a procedure that meets his needs for choosing the treatment processes applicable to particular waste streams. No matter how one approaches the problem of process selection, there are two seemingly conflicting criteria to keep in mind. The first is to *eliminate inappropriate processes* from consideration *at the earliest stage feasible*. The second is to *maintain an open mind for consideration of attractive processes as long as possible*.

B. BACKGROUND QUESTIONS FOR TREATMENT PROCESS SELECTION

- Nature of the Waste
    - What are the characteristics of the waste stream?
    - Is it a liquid, an emulsion, a slurry, a sludge, a solid powder, or a bulk solid?
    - What is its chemical composition?
    - Which components are potentially hazardous for land disposal; or more generally, what is the problem?
    - What are the physical properties of the waste stream – e.g., viscosity, melting point, boiling point, vapor pressure, Btu content, specific gravity, etc.?

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- Is the waste stream corrosive?
- Over what range will the typical physical and chemical properties vary?
- What is the volume or mass of waste that will require treatment from a typical plant and/or region?
- Where does the waste stream originate and at what points could it be intercepted for treatment?

Questions on the nature of the waste stream are asked for several reasons. One is to determine whether the waste stream characteristics match the feed stream requirements for various treatment processes. In a positive sense, this may be of interest to select processes for further consideration; or in a negative sense, to rule out processes that are not and could not be made useful for the particular waste under any circumstances. Another is to determine whether the waste stream is compatible with typical treatment process equipment, materials of construction, pumps, throughput rates, temperature, size of pipes, etc. A third, reflected in the last question, is to determine whether air and water pollution controls, or the method of waste collection used, might in fact create a stream which is more difficult to treat than the waste originally generated in the manufacturing operation.

- Objectives of Treatment – Desired Characteristics of the Output Stream
  - What is the present treatment/disposal method and why is this unacceptable?
  - What are the objectives or goals of treatment, in order of priority, i.e., purification, resource recovery, detoxification, volume reduction, safe disposal to land, safe disposal to water, compliance with regulations ?
  - What are the air, water and other environmental quality regulations which must be complied with?
  - What must be removed to make the waste stream amenable to disposal? What level of removal is necessary; i.e., what are the maximum allowable concentrations in the output stream(s)?
  - What are the chemical and physical property requirements for recycle or reuse of the output streams?
  - What are the physical and chemical property requirements for disposal to land or water?

Questions on the desired characteristics of the output streams are asked to: (1) clarify the objectives of a treatment process, (2) explicitly learn what regulatory standards must be met, (3) help establish criteria for judging the usefulness of various treatment alternatives in meeting the objectives; and (4) establish a bench mark for improvement by identifying current practice.

- Technical Adequacy of Treatment Alternatives
  - What processes, alone or in combination, are capable of meeting the treatment objectives?
  - If a sequence of processes is needed, are the processes technically compatible?
  - Can the key process selected for meeting the objectives handle the waste stream in its existing form? If not, can the waste stream be put into a form amenable to the process?
  - What key processes are really attractive technically?
  - Are there any components of the waste stream that would inhibit application of an otherwise technically attractive key process? Can these potentially inhibiting effects be minimized or eliminated?
  - If no process, as presently conceived, can meet the objectives, can any process be modified to do the job?
  - What function can each process perform, and how can the processes be grouped to achieve the objectives?
  - Are there any processes that must be eliminated on technical grounds?

Questions about technical adequacy are asked to help distinguish processes that are technically feasible for use on the waste from those that are totally infeasible treatment alternatives.

- Economic Considerations
  - What are the capital investment requirements for process implementation?
  - What are the operating costs?

- To what extent will credit for recovered material help offset operating costs?
- How do projected costs for alternative treatments compare with current costs of disposal and with each other?
- If recovery was an objective, is there enough value in the potentially recoverable material to be worthwhile?
- Are the technically optimal operating parameters in the proper range for economic operation of apparently attractive processes?
- If process modifications are required, what will they cost?
- For technically and operationally acceptable processes with equal operating costs (including capital amortization), is there any economic reason to prefer the lowest capital cost alternative?
- What is the cost impact of any necessary environmental controls?

From the industry point of view, economic questions are paramount in selecting alternative treatment methods for in-plant use and in choosing a waste treatment contractor.

- Environmental Considerations
  - Will air pollution control devices be required to clean up effluents?
  - Will output streams require clean-up prior to discharge into water bodies?
  - Will secured chemical landfill areas be necessary for solid residue(s) from process?

Waste treatment processes, like any manufacturing process, almost always result in some residue for disposal. Environmental questions are directed towards tracing the fate of the hazardous components present in the waste feed stream to the point of ultimate disposal.

- Energy Considerations
  - What are the energy requirements for process operation?
  - What form(s) of energy will be used, i.e., electricity, natural gas, oil, coal, etc.?

- Are estimated energy costs more than 10% of operating costs?

Questions of energy utilization are asked in order to assure that treatment processes satisfy current national objectives of both environmental protection and energy conservation. Both the absolute quantity of energy required and the form of the energy required are important. Energy-intensive processes generally would be in disfavor, unless there are compensating benefits (e.g., materials recovery). Processes that use natural gas, which is in short supply, might be particularly unattractive. The economics of treatment processes for which energy costs represent a significant fraction of operating costs would, of course, be tied to the price of fuel, which has in the recent past been quite volatile.

- Overall Evaluation
  - What factors are most important in selecting a treatment process?
  - Are there any standard, state-of-the-art processes that can be used for baseline comparisons?
  - Are costs "reasonable"?
  - Does any process have clearly desirable (or undesirable) features that make it attractive (or unattractive) for treating a particular waste stream?

The final choice of a treatment system, or t[illegible]ent process sequence, for a given waste stream involves engineering judgment, which [illegible] always highly subjective. The individual faced with the choice must not only establish his/her own selection criteria, but also weight those criteria in accordance with personal priorities. Questions asked in an attempt to make an overall evaluation, therefore, are directed towards a determination of the degree to which the objective features of alternative treatment systems meet subjective needs.

C. EXAMPLES OF PROCESS SELECTION PROCEDURES

1. Selection Based on the Nature of the Hazardous Wastes

For the purposes of identifying possible treatment processes, and eliminating those that are not likely to prove useful, a given waste stream is conveniently characterized with respect to three broad dimensions:

(a) *Physical form* – Is the waste stream as generated a:

- liquid?
- emulsion?
- pumpable slurry?

  - colloidal or non-colloidal?
- non-pumpable sludge?
- tar?
- bulk solid?
- powdered solid?

(b) *Hazardous components* – Does the waste stream contain:

- heavy "metal" cations (Sb, As, Cd, Cr, Hg, Pb, Zn, Ni, Cu, V, P, Be, Se, Mn, Ti, Sn, Ba, etc.)?
- heavy metal anions (chromates, chromites, arsenates, arsenites, etc.)?
- non-metallic toxic anions (cyanides, sulfites, thiocyanates, etc.)?
- organics (hydrocarbons, organic acids, organic peroxides, esters, alcohols, aldehydes, phenols, chlorocarbons, amines, anilines, pyridines, organic sulfur compounds, organic phosphorus compounds, alkaloids, sterols, etc.)?

(c) *Other properties* – For example,

- Is the liquid phase primarily aqueous or non-aqueous?
- What is the concentration of each of the hazardous components in each of the phases present?
- What are the non-hazardous components in each phase?

For a given waste stream, characterized by physical form and hazardous components, the matrix presented in Table 7 may be used to select potentially applicable treatment processes. For example, liquid ion exchange (LIE) might be capable of removing heavy metals from solid powders. The matrix in Table 8 focusses on processes that are *inapplicable* for given waste streams. It provides some guidance for ruling out processes that are not likely to be technically feasible for certain types of waste streams.

2. Process Selection Based on Desired Characteristics of the Output Streams

The output streams from any given treatment process may or may not be suitable for reuse or amenable to disposal without further treatment. In evaluating and analyzing treatment processes that might be applicable to particular waste streams, it is usually necessary at some stage to define the objectives of treatment and the desired characteristics of the output streams.

TABLE 7

TREATMENT PROCESSES FOR HAZARDOUS COMPONENTS IN WASTE STREAMS OF VARIOUS PHYSICAL FORMS

Physical Form	Treatment Processes* Heavy "metal" cations* and metal anions**	Non-metal anions***	Organics
Liquid	(IE), (FC), (UF), (ED), (RO), (Red), (LIE), (Ppt), (E1)	(CA), (LIE), (FC), (UF), (ED), (Oz), (RO), (Ox), (E1)	(CA), (RA), (Dis), (IE), (AS), (SS), (UF), (SE), (RO), (Ox), (Oz), (Hy), (C1), (MW), (Pb), (UF)
Emulsion	(UF)		
Slurry	(FC), (UF), (Red), (HGMS)	(FC), (UF), (Ox)	(Dis), (AS), (SS), (UF), (Oz), (Hy)
Sludge	(LIE), (FC), (Red)	(FC), (Ox)	(Dis), (Cal), (Oz), (Hy), (Ox)
Tar	(Cal)	(Cal)	(Cal), (Hy)
Bulk Solid	(Cal)	(Cal)	(Cal)
Solid Powder	(LIE)	(Cal)	(Cal), (Hy)

Legend:

(AS)	Air Stripping
(CA)	Carbon Adsorption
(Cal)	Calcination
(C1)	Chlorinolysis
(Dis)	Distillation
(ED)	Electrodialysis
(E1)	Electrolysis
(FC)	Freeze Crystallization
(HGMS)	High-Gradient Magnetic Separation
(Hy)	Hydrolysis
(IE)	Ion Exchange
(LIE)	Liquid Ion Exchange
(MW)	Microwave Discharge
(Ox)	Oxidation
(Oz)	Ozonation
(Ph)	Photolysis
(Ppt)	Precipitation
(RA)	Resin Adsorption
(Red)	Reduction
(RO)	Reverse Osmosis
(SE)	Solvent Extraction
(SS)	Steam Stripping
(UF)	Ultrafiltration

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*e.g., Sb, As, Cd, Cr, Hg, Pb, Zn, Ni, Co, V, P,Be, Se, Mn, Ti, Sn, Ba

**e.g., chromates, arsenates, arsenites, vanadates

***e.g., cyanides, sulfides, fluorides, hypochlorites, thiocyanates

TABLE 8

APPLICABILITY OF TREATMENT PROCESSES TO PHYSICAL FORM OF WASTE

	Single Phase				Two Phases	
		Liquid				
	Solid	Inorganic	Organic	Mixed	Slurry*	Sludge
1. Phase Separation Processes						
Filtration	n	n	n	n	y	n
Sedimentation	n	n	n	n	y	n
Flocculation	n	n	n	n	n	n
Centrifugation	n	n	n	n	y	n
Distillation	n	n	n	n	y	y
Evaporation	n	n	n	n	y	y
Flotation	n	n	n	n	y	n
Ultrafiltration	n	n	n	n	n	n
HGMS	p	n	n	n	n	n
Precipitation	n	n	n	n	n	n
2. Component Separation Processes						
Ion Exchange	n	y	y	y	n	n
Liquid Ion Exchange	y	y	y	n	y	y
Freeze Crystallization	n	y	y	n	y	y
Reverse Osmosis	n	y	n	y	n	n
Carbon Adsorption	n	y	n	y	n	n
Resin Adsorption	n	y	n	y	n	n
Electrodialysis	n	y	n	y	n	n
Air Stripping	n	n	y	y	y	n
Steam Stripping	y	n	y	y	y	n
Ammonia Stripping	y	y	n	n	n	n
Ultrafiltration	n	y	y	y	n	n
Solvent Extraction	p	y	y	y	n	n
Reverse Osmosis	n	y	n	y	n	n
Distillation	n	n	y	y	y	y
Evaporation	n	y	y	y	y	y
3. Chemical Transformation Processes						
Neutralization	n	y	y	y	y	y
Precipitation	n	y	y	y	n	n
Hydrolysis	p	n	y	y	y	y
Oxidation	n	y	y	y	n	n
Reduction	n	y	y	y	n	n
Ozonolysis	n	y	y	y	n	n
Calcination	y	y	y	y	y	y
Chlorinolysis	n	n	y	y	n	n
Electrolysis	n	y	n	y	n	n
Microwave	n	n	y	y	n	n
Biological	n	n	y	y	y	y
Catalysis	n	y	y	y	n	n
Photolysis	n	n	y	y	n	n

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*Slurry is defined here as a pumpable mixture of solids and liquids.

y = yes, workable; n = no; p = possible.

For example, if the treatment objective is to convert the given waste stream to one or more streams which can legally be discharged to a water body, the Federal and local water pollution control regulations will govern the characteristics of the output streams. If the treatment objective is recovery, those processes must be sought which either lead directly to a reusable resource, or which convert the waste to a form from which resources may be more easily recovered.

Table 9 provides some general characteristics of the output streams (end products) from various processes to aid in assessing their capability, alone or in combination, to meet defined objectives. Where processes are routinely or conveniently used in combination, follow-on steps are suggested, predicated on the assumption that the only hazardous components in the waste stream are those that the process listed can act on. If, for example, a waste stream containing both low-molecular-weight organic and heavy metal contaminants were treated by reverse osmosis, only the heavy metals would be concentrated in one of the output streams (RO1), and the other output stream (RO2) would have to be treated further to remove or detoxify the organics.

3. Selection Based on Technical and Operational Adequacy of Treatment Alternative

Table 7 shows that there are a number of treatment alternatives for various types of hazardous components in waste streams of different physical form. Tables 4-6 show further that several of the alternatives function similarly; i.e., they remove or detoxify certain types of hazardous components. All processes which function similarly on similar types of waste streams are not necessarily technically equivalent, however. The allowable feed stream concentrations may differ. The treatment efficiencies and hence concentration of hazardous components in the output streams may differ. The degree of interference by other components in the waste stream may differ. Throughputs may differ and the available experience with using the processes to treat hazardous wastes may also differ.

Table 10 compares treatment processes capable of separating heavy metals from liquid waste streams with respect to feed stream properties, output parameters and state-of-the-art. Tables 11-13 provide similar comparisons for processes that separate organics from liquids and toxic anions from liquids. Table 14 compares processes (other than phase separation processes) that can accept feed streams in the form of slurries or sludges. Table 15 compares processes that can accept feed streams in the form of tars, bulk solids or solid powders.

It is clear that the vast majority of processes considered in this program operate mainly on liquids. Some have potential for handling slurries and sludges, but in most real cases, a liquid/solid separation would precede treatment and/or disposal. None of the processes can directly treat bulk solids contaminated by heavy metals, such as slags from the metallurgical industries (an enormously large waste stream in the aggregate). Few processes can work directly on tarry or even powdered solid feeds. Unfortunately, water treatment sludges, still bottom tars, powdered particulate from air pollution control devices and oil-contaminated solids account for a larger fraction of the wastes destined for land disposal than do liquids.

TABLE 9

GENERAL CHARACTERISTICS OF THE END-PRODUCTS OF TREATMENT PROCESSES

Treatment		Output Streams			Possible Follow-On Steps
Type	Process	Code No.	Form	Characteristics	
1. Phase Separation	Filtration	F 1	Sludge	15-20% solids	Landfill, Calcination
		F 2	Liquid	500-5000 ppm total dissolved solids	Component Separation
	Sedimentation Centrifugation	S 1	Sludge	2-15% solids	Decantation
		S 2	Liquid	10-200 ppm suspended solids	
	Flotation	Fl 1	Stabilized	particle-bearing froth	Skimming
		Fl 2	Liquid	solution	Component Separation
	HGMS	H 1	Slurry	magnetic and paramagnetic particles	Recovery
		H 2	Liquid	solution	Component Separation
	Flocculation	Fc	Sludge or Slurry	flocculated particulates	Sedimentation, Filtration, Centrifugation
	Distillation	Dis 1	Sludge	still bottoms	Calcination
		Dis 2	Liquid	pure solvent	Sale
	Evaporation	E 1	Solid	—	Resource Recovery
			Liquid	condensate	Recovery or Disposal
2. Component Separation					
a. Inorganics	Ion Exchange	IE 1	Liquid	concentrated solution of hazardous components	Precipitation, Recycle, Electrolysis
		IE 2	Liquid	purified water with hazardous components at ppm levels	Discharge
	Liquid Ion Exchange	Similar to Ion Exchange			
	Carbon Adsorption	CA 1	Solid	adsorbate on carbon	Chemical Regeneration
		CA 2	Liquid	purified water	Discharge
	Reverse Osmosis	RO 1	Liquid	concentrated solution of hazardous components	Precipitation, Electrolysis, Recycle
		RO 2	Liquid	purified solution, TDS > 5 ppm	To Water Treatment

TABLE 9 (Continued)

Treatment		Output Streams			Possible Follow-On Steps
Type	Process	Code No.	Form	Characteristics	
	Electrodialysis	ED 1	Liquid	concentrated stream, 100-500 ppm salts	Precipitation, Metal Recovery
		ED 2	Liquid	dilute stream	To Water Treatment
	Freeze Crystallization	FC 1	Sludge	concentrated brine	Recovery
		FC 2	Liquid	purified stream, ~ 100 TDS	To Water Treatment
b. Organics	Carbon Adsorption	CA 1	Solid	adsorbate on carbon	Thermal or Chemical Regeneration
		CA 2	Liquid	purified water	Discharge
	Resin Adsorption	RA 1	Solid	adsorbate on resin	Solvent Regeneration
			Liquid	purified water, < 10 ppm organics	To Water Treatment
	Steam Stripping	SS 1	Liquid	aqueous steam concentrated in volatile organics	Recovery; Incineration
			Liquid	dilute aqueous stream with 50-100 ppm organics	To Water Treatment
	Solvent Extraction	SE 1	Liquid	concentrated solution of hazardous components in extraction solvent	Recovery of Extraction Solvent
		SE 2	Liquid	purified liquid; hazardous component concentration < 10 ppm	Recycle or Discharge
	Distillation	Dis 1	Sludge	still bottoms	Incineration
		Dis 2	Liquid	pure liquid	Sale
3. Chemical Transformation					
	Neutralization	N	Unchanged	stream of altered pH	Component Separation
	Precipitation	Ppt 1	Sludge	–	Landfill, Calcination
		Ppt 2	Liquid	supernatant with concentrations governed by solubility of precipitate	Depends on Product Stream Composition
	Oxidation Ozonation	O	Liquid	CO_2, H_2O and other oxidation products	Depends on Product Stream Composition
	Reduction	R	Slurry	heavy metals and residual reducing agent	Filtration

TABLE 9 (Continued)

Treatment		Output Streams			Possible Follow-On Stream
Type	Process	Code No.	Form	Characteristics	
	Calcination	Cal 1	Solid	oxide and/or other residue	Landfill or Recovery
		Cal 2	Gas	volatiles (CO_2, NO_x, SO_x, hydrocarbons, fine particulates)	Wet Scrubbing
	Hydrolysis	Hy	Liquid, Slurry or Sludge	mixture of products that may or may not be toxic	Resource Recovery
	Electrolysis	El 1	–	cathode reaction products	Often a Recovered Metal
		El 2	–	anode reaction products	Depends on Nature of Products
	Photolysis	P	Liquid	solution of photodecomposition products	Depends on Nature of Products
	Microwave Discharge	M	Gas	similar to incinerator emissions	Wet Scrubbing
	Catalysis	Depends on Reaction Catalyzed			
4. Biological Treatment					
	Activated Sludge	AC 1	Liquid	clean water	Discharge
		AC 2	Sludge	heavy metals and refractory organics	Calcination
	Aerated Lagoon				
	Trickling Filter				
	Waste Stabilization Pond	W	Liquid	clear water	Discharge
	Anaerobic Digestion	An 1	Sludge	–	Incineration
		An 2	Gas	CO_2, methane	Fuel Recovery
	Composting	Com 1	Sludge	concentrated in metals	Calcination or Recovery
		Com 2	Liquid	leachate solution of partially degraded organics	Component Separation

TABLE 10

COMPARISON OF PROCESSES THAT SEPARATE HEAVY METALS FROM LIQUID WASTE STREAMS

Process	State-of-the-Art	Required Feed Stream Properties	Characteristics of Output Stream(s)
Physical Removal			
Ion Exchange	Used but not common (Cat. IV)	Con. < 4000 ppm; aqueous solutions, low SS	One concentrated in heavy metals; one purified
Reverse Osmosis	Cat. IV	Con. > 400 ppm; aqueous solutions; controlled pH; low SS; no strong oxidants	One concentrated in heavy metals, one with heavy metal concentrations > 5 ppm
Electrodialysis	Cat. IV	Aqueous solutions; neutral or slightly acidic; Fe and Mn < 0.3 ppm; Cu < 400 ppm	One with 1000-5000 ppm heavy metals; one with 100-500 ppm heavy metals
Liquid Ion Exchange	Cat. IV	Aqueous solutions; no concentration limits; no surfactants; SS $< 0.1\%$	Extraction solvent concentrated in heavy metals; purified water or slurry
Freeze Crystallization	Needs development (Cat. III)	Aqueous solutions; TDS $< 10\%$	Concentrated brine or sludge; purified water, TDS ~ 100 ppm
Chemical Removal			
Precipitation	Common (Cat. V)	Aqueous or low viscosity non-aqueous solutions; no concentration limits	Precipitated heavy metal sulfides, hydroxides, oxides, etc.; solvent with TDS governed by solubility product of precipitates
Reduction	Cat. IV	Aqueous solutions; concentrations of heavy metals $< 1\%$; controlled pH	Acidic solutions with reagent (oxidized $NaBH_4$ or Zn); metallic precipitates
Electrolysis	Cat. III	Aqueous solutions; heavy metal concentrations $< 10\%$	Recovered metals; solution with 2-10 ppm heavy metals

TABLE 11

COMPARISON OF TREATMENT PROCESSES THAT SEPARATE ORGANICS FROM LIQUID WASTE STREAMS

Treatment Process	State-of-the-Art	Required Feed Stream Properties	Characteristics of Output Stream(s)
Carbon Adsorption	Used but not common (Cat. IV)	Aqueous solutions; concentrations $< 1\%$; SS < 50 ppm	Adsorbate on carbon; usually regenerated thermally or chemically
Resin Adsorption	Cat. IV	Aqueous solutions; concentrations $< 8\%$; SS < 50 ppm; no oxidants	Adsorbate on resin; always chemically regenerated
Ultrafiltration	Cat. IV	Solution or colloidal suspension of high molecular weight organics	One concentrated in high molecular weight organics; one containing dissolved ions
Air Stripping	Cat. IV	Solution continuing ammonia; high pH	Ammonia vapor in air
Steam Stripping	Cat. IV	Aqueous solutions of volatile organics	Concentrated aqueous streams with volatile organics and dilute stream with residuals
Solvent Extraction	Cat. IV	Aqueous or non-aqueous solutions; concentration $< 10\%$	Concentrated solution of organics in extraction solvent
Distillation	Cat. IV	Aqueous or non-aqueous solutions; high organic concentrations	Recovered solvent; still bottom liquids, sludges and tars
Steam Distillation	Cat. IV	Volatile organics, non-reactive with water or steam	Recovered volatiles plus condensed steam with traces of volatiles

TABLE 12

PROCESSES THAT DESTROY ORGANICS

Process	State-of-the-Art	Required Feed Stream Properties	Characteristics of Output Stream(s)
Biodegradation	Cat. V	Dilute aqueous streams with soluble organics	Pure water
Oxidation	Cat. IV	Dilute aqueous solutions of phenols, organic sulfur compounds, chlorinated hydrocarbons, etc.	Oxidation products in aqueous solutions
Ozonation	Cat. IV	Aqueous solutions; concentrations < 1%	Oxidation products in aqueous solutions
Calcination	Cat. IV	Organics and inorganics that decompose thermally	Solid oxides; volatile emissions
Hydrolysis	Needs development (Cat. III)	Aqueous or non-aqueous streams; no concentration limits	Hydrolysis products
Photolysis	Needs research (Cat. II)	Aqueous streams; transparent to light; components that absorb radiation	Photolysis products
Chlorinolysis	Cat. III	Chlorinated hydrocarbon waste streams; low sulfur; low oxygen; can contain benzene and other aromatics; no solids; no tars	Carbon tetrachloride; HCl and phosgene
Microwave Discharge	Cat. II	Organic liquids or vapors	Discharge products; not accurately predictable

TABLE 13

COMPARISON OF PROCESSES THAT SEPARATE TOXIC ANIONS FROM LIQUID WASTE STREAMS

Process	**State-of-the-Art**	**Required Feed Stream Properties**	**Characteristics of Output Stream(s)**
Physical Removal			
Ion Exchange	Cat. IV	Inorganic or organic anions in aqueous solution	Concentrated aqueous solutions
Liquid Ion Exchange	Cat. IV	Inorganic or organic anions in aqueous solution	Concentrated solutions in extraction solvent
Electrodialysis	Cat. IV	Aqueous stream with 1000-5000 ppm inorganic salts; and pH; Fe and Mn < 0.3 ppm	Concentrated aqueous stream (10,000 ppm salts); dilute stream (100-500 ppm salts)
Reverse Osmosis	Cat. IV	Aqueous solutions with up to 34,000 ppm total dissolved solids	Dilute solution (~ 5 ppm TDS); concentrated solution of hazardous components
Freeze Crystallization	Needs development (Cat. III)	Aqueous salt solutions	Purified water; concentrated brine
Chemical Removal			
Oxidation	Cat. III-IV	Aqueous solutions of cyanides, sulfides, sulfites etc.; concentrations $< 1\%$	Oxidation products
Ozonation	Cat. IV	Aqueous solutions of cyanides; concentrations $< 1\%$	Cyanate solutions
Electrolysis	Cat. III	Alkaline aqueous solutions of cyanides or concentrated HCl solutions ($>20\%$)	Cyanides to ammonium and carbonate salt solutions; HCl to Cl_2 gas

TABLE 14

COMPARISON OF PROCESSES THAT CAN ACCEPT SLURRIES OR SLUDGES

Process	State-of-the-Art	Required Feed Stream Properties	Characteristics of Output Stream(s)
Calcination	Used but not common (Cat. IV)	Waste stream with components that decompose by volatilization (hydroxides, carbonates, nitrates, sulfites, sulfates)	Solid greatly reduced in volume; volatiles
Freeze Crystallization	Needs development (Cat. III)	Low-viscosity aqueous slurry or sludge	Brine sludge; purified water
HGMS	Needs research (Cat. II)	Magnetic or paramagnetic particles in slurry	Particles adsorbed on magnetic filter
Liquid Ion Exchange	Cat. IV	Solvent extractable inorganic component	Solution in extraction solvent
Flotation	Cat. III	Flotable particles in slurry	Froth
Hydrolysis	Cat. II	Hydrolyzable component	Hydrolysis products
Anaerobic Digestion	Cat. IV	Aqueous slurry; $< 7\%$ solids; no oils or greases; no aromatics or long chain hydrocarbons	Sludges; methane and CO_2
Composting	Cat. IV	Aqueous sludge; $< 50\%$ solids	Sludge; leachate
Steam Distillation	Cat. IV	Sludge or slurry with volatile organics	Volatile, solid residue
Solvent Extraction	Cat. IV	Solvent extractable organic	Solution of extracted components; residual sludge

TABLE 15

COMPARISON OF PROCESSES THAT CAN ACCEPT TARS OR SOLIDS

Process	State-of-the-Art	Required Feed Stream Properties	Characteristics of Output Stream(s)
Calcination	Used but not common (Cat. IV)	Tars or solids that can be volatilized	Volatiles; char and/or metal oxides
Hydrolysis	Needs development (Cat. III)	Tars or solid powders	Hydrolysis products
Steam Distillation	Cat. IV	Solids contaminated with volatile organics	Purified solids; condensed organics
Dissolution	Cat. IV	Tars, solids, or solid powders that will dissolve in some reagent	Liquid solution for further treatment; solid residue
Crushing and Grinding	Cat. IV	Bulk solid	Powdered solid
Cryogenics	Needs research (Cat. II)	Tar, bulk solid	Reduced particle size

Crushing and grinding, and dissolution are therefore likely to play important roles in subsequent design of alternative hazardous waste treatment systems. Tars, which are often neither easy to crush and grind nor to dissolve, might be reduced to smaller particle size by cryogenic cooling. The smaller particles thus formed should dissolve more rapidly than the bulk tar removed from the reactor.

4. Selection on the Basis of Economic Considerations

Processes performing similar functions are compared with respect to capital and operating costs in Table 16. The bases for the cost estimates are summarized in the Preface to Part Two. For more detailed descriptions of the types of waste streams assumed in developing the costs in Table 15, refer to the individual process reports. In deriving costs of alternative treatment systems (generally a sequence of processes) for any given waste stream, operating parameters specific to the particular situation should be taken into account; the costs in Table 16 and the economic analyses given in Part Two only provide general guidelines.

TABLE 16

APPROXIMATE TREATMENT COSTS

Process	Annual Volume or Mass of Waste Stream Treated (typical), gpd	Capital Costs	Operating Costs	Fraction of Operating Costs Attributable to:			
				Labor	Energy	Materials	Other*
Phase Separation							
Sedimentation	5,000,000	–	$0.10-0.50/1000 gal	–	–	–	–
Vacuum Filtration	36,000	$ 200,000	$5-7/1000 gal	45	4	1	50
Centrifugation	36,000	$ 140,000	$5-7/1000 gal	35	5	17	43
Freeze Crystallization	50,000	$ 280,000	$6-12/1000 gal	52	16	–	32
Evaporation	20,000,000	$1,300,000	$1-2/1000 gal	3	92	–	5
Metal Removal From Liquids							
Precipitation	400,000	$ 300,000	$1-2/1000 gal	47	2	5	46
Electrodialysis	9,000	$ 24,000	$5-7/1000 gal	62	3	7	28
Ion Exchange	80,000	$ 400,000	$4-6/1000 gal	36	2	46	16
Liquid Ion Exchange	80,000	$ 300,000	$3-5/1000 gal	24	1	12	63
Reduction	2,000	$ 230,000	$150-200/1000 gal	32	21	15	32
Reverse Osmosis	3,000	$ 12,000	$9-11/1000 gal	29	6	–	65
Electrolysis	20,000	$ 31,000	$1-2/1000 gal	–	10-35	–	–
Organic Removal From Liquids							
Carbon Adsorption	100,000	$1,200,000	$5-20/1000 gal (high figure with regeneration)	24	5-25 (high with thermal regeneration)	15	36-56
Resin Adsorption	67,000	$ 720,000	$11-13/1000 gal	11	40	Regenerating Solvent recovered	
Solvent Extraction	100,000	$ 400,000	$4-6/1000 gal				
Steam Stripping	720,000	$ 500,000-850,000	~$10	2	72	–	21
Steam Distillation	750	$ 130,000	$0.25-0.90/1000 gal	53	6	–	41
Distillation	1,000	$ 230,000	$264/1000 gal	14	12	–	74
Hydrolysis	30,000	$ 320,000	$20-30/1000 gal	57	17	–	26
Oxidation	1,000	$ 100,000	$229/1000 gal	44	4	15	37
Ozonation	800,000	$ 330,000	$0.40-1.00/1000 gal	26	20	–	54
Other							
Neutralization	1,000,000	$1,050,000	$2-3/1000 gal	15	1.5	59	24.5
Calcination	156,000	$2,900,000	$15-20/1000 gal	10	26	–	64
Chlorinolysis	20,000	$5,500,000	$3000/1000 gal	1	4	88	7

*Capital amortization, water, maintenance, etc.

V. WASTE TREATMENT PROCESS SUMMARIES

The following pages summarize briefly the salient features of each of the treatment process considered. More complete process descriptions are provided in Part Two.

ADSORPTION, CARBON

I. CONCLUSIONS AND RECOMMENDATIONS

Carbon adsorption should be given serious consideration whenever it is desirable to remove mixed organics, or to recover select organic or inorganic species from aqueous waste streams with adsorbate concentrations less than 1%.

II. PROCESS DESCRIPTION

A large variety of organic solutes, and a more limited number of inorganic solutes can be removed from aqueous waste streams by adsorption onto activated carbons with a high absorptive surface area (500-1500 m^2/g). Adsorption of organic solutes is commonly followed by thermal regeneration of the carbon and simultaneous destruction of the absorbates. In a few cases, the carbon may be regenerated and the adsorbate recovered by treatment with acid, base, steam, or solvent.

III. APPLICATIONS TO DATE

There are about 100 full-scale carbon adsorption systems currently in use for industrial/municipal wastewater treatment. In general, the process works best with chemicals that have a low water solubility, high molecular weight, low polarity, and low degree of ionization. The concentration of adsorbates in the influent should be less than 1%, and suspended solids must be low ($\lesssim$50 ppm) for most systems. Recovery is possible if the adsorbate may be easily volatilized or dissolved off the carbon. Thermal regeneration (with organic adsorbates) is economical if the carbon usage is above about 1000 lb/day.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements include electricity for pumps and fuel for the regeneration furnace. Energy costs may be around 25% (or higher) of the total operating costs where concentrated waste streams are being treated and the carbon is thermally regenerated. Energy may constitute no more than 5% of total operating costs if regeneration is accomplished by non-thermal means.

Capital costs for a 100,000-gpd facility would be in the neighborhood of $1,000,000. Total operating costs would be in the range of $5-20/1000 gal.

If spent carbon is not regenerated, it presents a problem for disposal. If it is thermally regenerated, the regeneration furnace will usually require an afterburner, a scrubber, and perhaps a dust filter.

V. OUTLOOK FOR WASTES

For aqueous waste streams containing up to 1% of refractory or toxic organics, carbon adsorption is an excellent, proven process. For more concentrated waste streams, solute removal would be even more efficient, but the more frequent regeneration required would significantly increase costs. Development of new methods of regeneration, particularly ones that allow recovery of the adsorbate, could greatly expand potential applications of the process.

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ADSORPTION, RESIN

I. CONCLUSIONS AND RECOMMENDATIONS

Resin adsorption, like carbon adsorption, is a useful process for extraction of organic solutes from aqueous waste streams. Resin adsorption will generally be preferred when it is desirable to recover the adsorbate. Carbons are usually thermally regenerated with destruction of the adsorbate. Resins are always chemically regenerated (with caustic or organic solvents).

II. PROCESS DESCRIPTION

Resin adsorption uses synthetic resins (which can vary significantly in their chemical and physical nature) to extract and recover, if desired, dissolved organic solutes from aqueous waste streams. Resins with either (or mixed) hydrophobic or hydrophylic natures are available, and can be used to extract, respectively, hydrophobic or hydrophylic solutes. Resins are always chemically regenerated. When organic solvents are used as the regenerant, solute recovery is generally via distillation.

III. APPLICATIONS TO DATE

Current industrial waste treatment applications include: phenol recovery; color removal; and fat removal from aqueous waste streams. The phenol concentration can be as high as 8% by weight in the feed.

Proposed waste treatment applications (near-term) include removal of toxic chemicals from munitions facilities' effluents; removal of pesticides from aqueous streams; carcinogen removal from laboratory waste waters; and removal of phenolics; and removal of chlorinated hydrocarbons.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are small when the regenerant is not recycled. When both solvent and solute are recovered, the steam requirements for distillation (up to three stills required) will be significant. If the regenerant is not recycled, it must be disposed of. If the regenerant is recycled (e.g., by distillation), the still bottoms must be disposed.

Capital costs are moderately large; while no furnace is needed for regeneration (an expensive item with carbon systems), resins costs are high. Operating costs may be below $1/1000 gal in some applications, but may reach $5-20/100 gal when concentrated waste streams are treated and the solute recovered. Credit for recovered solute can allow a system to operate at a profit in favorable cases.

V. OUTLOOK FOR WASTES

Resin adsorption is particularly attractive for removing organics from aqueous waste streams when material recovery is desirable, and when the waste stream contains high levels of dissolved inorganic salts. Applications appear to be expanding.

BIOLOGICAL TREATMENT: ACTIVATED SLUDGE

I. CONCLUSIONS AND RECOMMENDATIONS

Activated sludge treatment is extensively used in industry, and is probably the most cost-effective method of destroying organics present in an aqueous waste stream. Neutralization and equalization of the waste stream, as well as suspended solids removal, should precede the activated sludge system. It is a safe and reliable process which is relatively uncomplicated to operate and relatively inexpensive. Improved understanding of activated sludge microbiology and enzyme catalysis will improve process operating efficiencies in the future.

II. PROCESS

Aqueous organic waste streams having less than 1% suspended solids have **flocculated**, biological growths continuously circulated and contacted in the presence of oxygen. Since the process was introduced at the turn of the century it has been modified through improved methods of maintaining aerobic conditions under varying organic loadings.

The process involves an aeration step, followed by solids-liquid separation, with recycle of a portion of the solids. The basic system has an open tank for the mixture of the active biomass with influent wastewater and air, followed by a clarifier. Bacteria in activated sludge systems serve to perform hydrolysis and oxidation reactions.

III. APPLICATIONS TO DATE

The activated sludge process has been applied extensively to treat wastewater from municipal sewage plants, canneries, paper and pulp mills, refineries, breweries, and steel, textile, petrochemical, pharmaceutical, and timber processing plants. It has also been applied to photo processing wastes and to the propylene glycol wastewater from polyvinyl chloride production.

IV. ENERGY, ENVIRONMENT, ECONOMICS

The activated sludge system is energy-intensive, with over 10% of total operating cost based on energy needed for pumping, aeration and clarification. The system is basically environmentally sound; no chemicals are added and natural degradation takes place.

Capital costs are about 10¢ per 1,000 gallons for a 10 mgd facility. These costs increase to over $1 for facilities handling less than 1 mgd. Processes handling dilute wastewaters are reported to have total costs of 10-40¢ per 1,000 gallons.

V. OUTLOOK FOR WASTES

Activated sludge systems are employed in at least two facilities for treatment of hazardous wastes. The system is environmentally sound because it employs natural microbial metabolic processes; no chemicals are added.

BIOLOGICAL TREATMENT: AERATED LAGOONS

I. CONCLUSIONS AND RECOMMENDATIONS

The aerated lagoon biological treatment process decomposes organics in wastewater containing less than 1% solids, employing essentially the same microbial reactions as activated sludge. The aerated lagoon, however, does not have a sludge recycle system for continuous circulation of microorganisms, and microbial strains do not acclimatize to the same extent. BOD removal efficiencies range from 60 to 90%. The process is not as attractive for industrial waste treatment as the activated sludge process; removal efficiencies are not as high and the process is less flexible in maintaining effluent limitations under varied influent loading.

II. PROCESS

The aerated lagoon technique developed from adding artificial aeration to existing waste stabilization ponds. Usually the lagoon is an earthen basin with sloping sides and about 6-17 feet depth. For the treatment of industrial wastes, it may be necessary to line the basin with an impermeable material. Because wastewaters in aerated lagoons are generally not as well mixed as those in activated sludge basins, a low level of suspended solids is maintained. If mixing and aeration are not complete, a portion of the solids settles to the bottom and undergoes anaerobic microbial decomposition. Retention times are slightly longer than for activated sludge; and where anaerobic decomposition is encouraged, the time is even longer.

III. APPLICATIONS TO DATE

The process has been successfully used for petrochemical, textile, pulp and paper mill, cannery, and refinery wastewaters.

IV. ENERGY, ENVIRONMENT, ECONOMICS

For comparable treatment efficiency, energy requirements are comparable to those for activated sludge treatment; but generally the aerated lagoon employs less energy for aeration and longer retention periods. Chemical requirements are essentially limited to addition of nutrients. As in activated sludge treatment, the effluent is a clarified liquid and a biomass sludge residue; the biosolids are more difficult to flocculate and settle from the mixed liquor because of the longer retention time.

Total costs range from 10 to 30¢/1000 gallons of dilute influent; if basin lining and high aeration is required, treatment costs may be nearly $2/1000 gallons.

V. OUTLOOK FOR WASTES

The process is not as attractive as activated sludge treatment for a wastewater influent with highly variable organic and metal concentrations.

BIOLOGICAL TREATMENT: ANAEROBIC DIGESTION

I. CONCLUSIONS AND RECOMMENDATIONS

Anaerobic digestion is a biological treatment process for the degradation of simple organics in an air-free environment. Part of the carbon substrate is used for cell growth and the other is converted to methane and carbon dioxide gas. The microbiology is complex and still not well understood. Two types of interdependent organisms are present, and steady-state environmental conditions must be maintained to keep them balanced. Because of this delicate balance, the process is not suitable for treatment of most industrial processing sludges. Oil, fat, and grease are also troublesome.

II. PROCESS

The organic sludges and biomass sludges from primary clarification and biological treatment are processed to reduce their volume and improve their stability. In the conventional process, the waste stream is fed into the middle zone of a closed tank with no agitating mechanism. The solids are digested by the organisms, gas rises, bringing scum to the surface, and the gas is collected from the roof of the tank. Usually this gas is used to maintain the temperature of the installation and sometimes to heat other parts of the plant. The digested sludge settles to the bottom of the tank after 30 to 60 days. There is only a small volume of digested sludge, which is stable and inert and can be disposed of for land reclamation or by ocean dumping. The bacteria are sensitive to pH, temperature, and the composition of the waste, but usually with time the system will achieve its own balance. Modifications have been made for some installations, usually involving agitation or heating, shortening the process to several days to two weeks.

III. APPLICATIONS TO DATE

Most installations have been for the digestion of sewage sludge, as the final step in a complete municipal waste treatment facility. Boston and Chicago both use anaerobic digesters: Boston disposes of the waste by ocean dumping; Chicago, whose plant is the world's largest, treating a billion gallons of wastewater per day, uses the waste for land reclamation. In the past 20 years, the system has been studied for meat packing wastes, and there are several plants operating commercially. It has also been studied for cotton kiering liquor, brewery wastes and alcohol distillery wastes.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy demands are relatively low; some electric power is needed to mix the reactor contents, recycle some of the effluent sludge to the reactor and heat the incoming sludge. Essentially all of the power for the heat exchanger is provided through production of methane gas.

The presence of arsenate or mercury in anaerobic digestors could lead to formation of toxic compounds.

In municipal wastewater treatment plants, costs for anaerobic digestion are difficult to segregate. Estimates for a facility treating 100,000 gal/day of sludge with 5% solids would be: capital investment, $1.25 million, annual fixed costs would be $219,000, and variable costs $171,000. The cost for treating 10^3 gallons would be $10.69.

V. OUTLOOK FOR WASTES

There seems to be a potential for disposal of feed lot wastes, culture material from pharmaceutical processing, and food processing wastes. For industrial processing sludges, the method may be suitable if there is a steady volume and flow, oil and grease are removed, and soluble metal content is low.

BIOLOGICAL TREATMENT: COMPOSTING

I. CONCLUSIONS AND RECOMMENDATIONS

Composting provides a means of achieving aerobic digestion of organic wastes by microorganisms in the presence of their own released heat. It is the only biological treatment process relatively insensitive to toxicants and it encourages adsorption of metals. Costs are higher than for other biological processes, but lower than for incineration.

II. PROCESS

Composting basically involves piling ground waste in windrows and aerating the piles by periodic turning. All that need be done is scheduling of spreading and turning with earthmoving equipment, adding some nutrients and alkalis if necessary, and providing for collection of leachate and runoff water to protect groundwater. There are over 30 process modifications involving rotating drums, forced aeration, etc. Complete digestion of most organic wastes take place in three or four months, although refinery wastes or other difficult organics may take up to a year.

III. APPLICATIONS TO DATE

Systematic composting has been widely used in Europe, where there is a ready market for composted waste as an organic soil conditioner. Most of the demonstration projects in the United States have closed for lack of a market for humus, but some cities use this cost-effective disposal technique for municipal refuse and give the compost away. Chicago uses the system to dispose of high-strength organic sludges, and several petroleum refineries use it for refinery wastes. It has also been used for cannery solids, pharmaceutical and meat packing sludges.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy demand is low, limited primarily to fuel costs to operate earthmoving equipment and pumps.

The only emissions from composting are carbon dioxide, steam, a liquid effluent containing partially oxidized organics and a barnyard smell indicative of healthy microbial activity.

Costs for composting are about $30/thousand gallons of influent, exclusive of land acquisition or further treatment of collected leachate. The capital expenditure to handle 100,000 gpd would be $1.5 million; fixed costs $275,000 annually and variable costs $802,500.

V. OUTLOOK FOR WASTES

Composting is applicable to high-organic wastes, including oils and tars and industrial processing sludges.

BIOLOGICAL TREATMENT: ENZYME TREATMENT

I. CONCLUSIONS AND RECOMMENDATIONS

Enzyme treatment of industrial processing wastes is totally impractical. Enzymes catalyze specific reactions and cannot adapt well to the varying composition of typical waste streams. Furthermore, enzyme production is very expensive.

II. PROCESS DESCRIPTION

Enzymes are highly selective chemical catalysts which act on specific molecules. The urease enzyme, for example, breaks down urea into carbon dioxide and ammonia. A hydrolase enzyme derived from yeast has been shown to oxidize phenol to carbon dioxide and water. The cellulose enzyme, produced by a stream of fungus, *Trichoderma viridi*, catalyzes the hydrolysis of cellulose to glucose.

III. APPLICATIONS TO DATE

There are no known full-scale applications of enzyme treatment processes in hazardous waste management. There are commercial applications in meat tenderizing, de-hairing of hides prior to tanning, cheese-making, pharmaceutical manufacture, and detergent production.

The Army's Natick Research and Development Command is operating a 1000 lb/mo. pilot plant to convert waste paper into glucose. A number of Government, university, and industrial laboratories are investigating the use of lactose for recovery of monosaccharides from cheese whey. Groups at Oak Ridge National Laboratories and the University of Pennsylvania have studied the enzyme decomposition of phenol.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Due to the specificity of enzyme reactions and the fact that current waste treatment applications are limited in number and lab scale, no useful generalizations can be made about energy, economics, or potential environmental impacts.

V. OUTLOOK FOR WASTES

Enzyme treatment may be useful for specialized industrial applications, particularly in cases where salable reaction products result. Enzymes have little or no potential in general waste treatment.

BIOLOGICAL TREATMENT: TRICKLING FILTERS

I. CONCLUSIONS AND RECOMMENDATIONS

The trickling filter process is a proven technology for the decomposition of organics in waste streams with less than 1% suspended solids. The process brings the wastewater in contact with aerobic microorganisms by trickling the water over media supporting the microorganisms. BOD removal efficiencies range from 50 to 85%. The process is used in industry to accept wastewater loading variations and provide a relatively uniform effluent for treatment by other biological processes, such as activated sludge.

II. PROCESS

Wastes are sprayed through the air to absorb oxygen, and then allowed to trickle through a bed of rock or synthetic media coated with a slime of microbial growth. Process modifications employ various media and depths to retain the microorganisms under varying hydraulic and effluent recycle conditions. The primarily metabolic processes are aerobic, and the microbial population is similar to the activated sludge population. However, because of the relatively short contact time, the percentage removal of organics is not as great.

The process involves open tanks or towers to house the filter packing, followed by effluent clarifiers. Recycle pumps may be used to recirculate filter effluent. A rotating spray dosing system feeds influent wastewater to the filter surface.

III. APPLICATIONS TO DATE

Trickling filters have been extensively used in sewage treatment and in treatment of refinery wastewaters containing oil, phenol, and sulfide. They are applicable to the same industrial waste streams as the activated sludge process, including cannery, pharmaceutical, and petrochemical wastes.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy demands are low, as little as one-tenth that of activated sludge treatment. Dilute wastewater is treated at a total cost between 10 to 30¢ per 1000 gallons; for concentrated waste requiring filter recycle the cost may be $2 per 1000 gallons. The process effluents are a liquid wastewater from which a major portion of the dissolved organics have been removed and a biomass sludge.

V. OUTLOOK FOR WASTES

The process could be used in sequence with other biological treatment, such as activated sludge, but it is not generally efficient enough to use as the sole method of biodegradation.

BIOLOGICAL TREATMENT: WASTE STABILIZATION PONDS

I. CONCLUSIONS AND RECOMMENDATIONS

Waste stabilization ponds utilize natural biodegradation reactions in wastewaters containing less than 0.1% solids with low concentrations of organics. The process is more sensitive to concentrations of inorganics and suspended solids than any of the other biological treatments discussed in this report. It is suitable for industrial wastes only where preliminary treatment has removed most contaminants and final effluent polishing is needed before discharge to a receiving water.

II. PROCESS

Waste stabilization ponds are large shallow basins where wind action provides aeration and a mixed autotrophic and heterotrophic microbial population provides decomposition of organics over a long retention time. Deep ponds, more than 4 feet deep, may promote anaerobic decomposition of settled sludge.

III. APPLICATIONS TO DATE

Waste stabilization ponds have been widely used for sanitary sewage and dilute industrial wastes, mostly to provide final effluent polishing. Industries using the method include meat and poultry packing, canneries, dairies, iron and steel works, paper and pulp mills, textile mills, oil refineries and petrochemical plants.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Large land acreage is the principal capital cost; energy and chemical requirements are insignificant. Total costs for treating dilute wastewaters in unlined basins range from 5 to 15¢ per 1000 gallons; for more concentrated waste streams in clay-lined basins, the cost is about $1.70 per 1000 gallons. Energy is needed only for pumping. A polished liquid effluent and some biomass sludge are the end-products.

V. OUTLOOK FOR WASTES

The process can be employed only where substantial land acreage is available and where climate is suitable. Toxic inorganics must be removed before waste stabilization ponding because of the system's high sensitivity to inhibitors. The use of the method for final polishing provides extra insurance that final effluent guideline limitations will be met.

CALCINATION

I. CONCLUSIONS AND RECOMMENDATIONS

Calcination is a well established process, and one of the few that can satisfactorily handle sludges. Calcination is recommended as a one-step process for treatment of complex wastes containing organic and/or inorganic components. The organics are destroyed; the inorganics are generally reduced in volume and converted into a form of low leachability suitable for landfill.

II. PROCESS DESCRIPTION

Calcination is a thermal decomposition process, generally operated around 1000°C at atmospheric pressure. It can be applied to aqueous solutions, slurries, sludges, and tars to drive off volatiles and to produce a dry powder or sintered solid. Typical calciners include the open hearth, rotary kiln, and fluidized bed.

III. APPLICATIONS TO DATE

Industrial applications include production of cement, lime, magnesia, titania, and wall plaster, and smelting of sulfide and carbonate ores. Waste treatment applications include recalcination of lime sludges from water treatment plants; coking of heavy residues and tars from petroleum refining operations; concentration and volume reduction of liquid radioactive wastes; and treatment of mixed refinery sludges containing hydrocarbons, phosphates, and compounds of Ca, Mg, K, Na, S, Fe, and Al.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are generally high, but depend on the water and organic content of the waste stream. Calcination of dry material requires about $1\text{-}3 \times 10^6$ Btu/ton of solid product; calcination of a sludge or slurry with 90% water requires about 20×10^6 Btu/ton of solid product. If this waste stream contains a combustible organic fraction, the energy requirements are reduced.

In general, calcination systems will require fairly extensive air pollution control equipment, including particulate-removal devices, wet scrubbers, and possibly final gas adsorption systems.

Capital investment costs for a calciner are in the range of $10,000-$30,000/ton of throughput daily. Operating costs are highly variable, depending on the water and organic content of the waste stream, and the possibilities for resource recovery credits.

V. OUTLOOK FOR WASTES

Calcination has been used widely in industrial and waste treatment applications. Its use is likely to expand, particularly in the treatment of tars, sludges, and other residues which present particularly difficult problems for disposal.

CATALYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Whenever a waste stream can usefully be treated by a chemical transformation process, the possibility of catalyzing the reaction should be considered. In general, if a transformation can be successfully catalyzed, operating costs and energy requirements will be reduced.

II. PROCESS DESCRIPTION

Catalysis is not a process in itself, but rather a modification of the rate or mechanism of chemical reaction processes through the use of catalysts, which are themselves unchanged at the end of a reaction.

III. APPLICATIONS TO DATE

The industrial applications of catalysts in the petroleum refining, chemical, pharmaceutical, and textile industries are legion.

In the field of waste treatment, catalytic oxidation is used quite widely as an alternative to incineration in the decomposition of waste organics. A number of catalytic processes have been investigated in the laboratory for destruction or detoxification of chlorinated pesticides, oxidation of cyanides, sulfides, and phenols, decomposition of sodium hypochlorite solutions, and conversion of mixed carboxylic acid waste streams to fumaric acids for recovery.

IV. ENERGY, ENVIRONMENT, ECONOMICS

In general, a catalytic process operates at a much lower temperature than the equivalent non-catalytic process and hence consumes less energy.

Environmental impacts are generally the same as those of the non-catalytic process.

Catalytic processes may be higher in capital costs than non-catalytic processes in some cases. However, the less severe operating conditions (lower temperatures and/or pressures) almost always result in lower overall operating costs.

V. OUTLOOK FOR WASTES

As the use of chemical processing in waste treatment increases, the effort to develop catalytic processes should be increased as well. A great deal of work is needed to demonstrate the commercial practicality of catalytic reactions tested in the laboratory, and exploratory work could be useful on catalytic hydrogenation and low-temperature air oxidation.

CENTRIFUGATION

I. CONCLUSIONS AND RECOMMENDATIONS

Centrifugation is a well-developed liquid/solid separation process being used in a variety of full-scale applications for material processing and waste treatment. In treating hazardous wastes, centrifugation can be used to greatest advantage to increase the solids concentration, and thereby reduce the volume, of a high concentration liquid/solid mixture (sludge) by partially separating the liquid and solid phases ("sludge dewatering").

Centrifugation is generally technically and economically competitive with other sludge dewatering processes (e.g., vacuum filtration or the use of filter presses) and should be considered as a potential process for concentrating hazardous waste sludges and slurries. Equipment is commercially available in a large variety of sizes and configurations.

II. PROCESS

Centrifugation is a physical process whereby the components of a fluid mixture are separated mechanically by the application of centrifugal force, applied by rapidly rotating the mass of fluid within the confines of a rigid vessel. Centrifugal forces acting on the revolving mass of fluid cause the solids suspended in the fluid to migrate to the periphery of the vessel where they can be separated. The particles are removed as a liquid/solid mixture significantly more concentrated than the original liquid.

III. APPLICATIONS TO DATE

Some common applications of centrifugation are in separating oil and water mixtures; clarification of viscous gums and resins; classification and removal of oversize particles and unground pigment from lacquers, enamel and dye paste; clarification of essential oils, extracts, and food products, such as homogenized milk and fruit juices; separation of micro-organisms from fermentation broths, recovery of finely divided metal such as silver from film scrap and platinum from spent catalyst; separation of acid sludges from the acid treatment of petroleum; recovery of crystalline solids from brine; dewatering of fibrous solids such as paper pulp and chemical fibers; dewatering and removal of starch from potato fibers, etc. Probably the main application for centrifuges at present is the dewatering of waste sludges.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Power requirements for centrifugation are typically 0.3-1.2 horsepower per gallon per minute of inlet waste feed. Power consumption is equal to or slightly greater than for other sludge dewatering processes.

For most sludge dewatering purposes, centrifugation is generally cost-competitive with other dewatering processes such as vacuum filtration or press filtration.

A conveyor bowl type centrifugation system capable of dewatering 6 tons per day of sludge (dry basis) will have an installed capital cost of approximately $140,000 and a total operating cost (including amortization) of $34.50 per ton of solids dewatered. In most applications, costs range from $20-$45/ton.

V. OUTLOOK FOR WASTES

The major application of centrifugation to waste treatment is the dewatering of waste sludges generated by water pollution control systems. Centrifuges have for many years been used on biological sludges from municipal treatment plants and from pulp and paper mills. Some expect the technique to replace vacuum filtration as the most common dewatering technique, especially for sticky or gelatinous sludges. It will also find further application in removing soluble metals from wastewater, as from the wet scrubbers used in the steel industry, to dewater sludges generated from sulfur dioxide air pollution control systems, etc.

Because it is capable of totally closed operation, centrifugation is particularly well suited to treating liquids that are volatile, flammable, or otherwise pose health and/or safety hazards to operating personnel.

CHLORINOLYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Chlorinolysis is capable of converting most liquid chlorinated hydrocarbons completely to carbon tetrachloride. It is not really a waste treatment process, but a manufacturing process that uses chlorocarbon waste streams and residuals as feedstocks. The process has excellent resource recovery potential (sufficient wastes are generated in the Gulf Coast region to support at least one 25,000 ton/yr chlorinolysis plant) if there is a market for the carbon tetrachloride. There may be, however, legal and institutional problems that might hinder transfer of wastes from generators to an operating chlorinolysis unit.

II. PROCESS

At temperatures around 500°C and pressures of about 200 atm in the presence of excess chlorine, the carbon-carbon bonds of hydrocarbons can be broken, and the molecules recombined to react with chlorine to form carbon tetrachloride. Because liquid chlorine is highly reactive, reactors and piping must be high-purity nickel, surrounded by a stainless steel jacket. The organic feedstock and preheated chlorine are introduced to the reactor, which is heated to initiate chlorinolysis; subsequently the process provides its own heat. At the end of the process, the pressure is released and the products are cooled and drawn off. Subsequent processing by distillation yields carbon tetrachloride, the principal product for sale.

III. APPLICATIONS TO DATE

This is not a waste treatment process, but a production process that can utilize waste streams. A semicommercial plant to produce 6000-8000 tons/year has been operating in Germany and a 50,000 ton/year plant is planned for the same site.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Electricity and fuel requirements per ton of carbon tetrachloride are relatively small – 135 kWh and 794 Btu, respectively. Chlorinolysis offers the opportunity of resource recovery, but the process involves hydrochloric acid and phosgene gas effluents. Neutralization of the effluent streams will produce sodium hypochlorite, which is toxic to aquatic life.

Capital and operating costs for a plant processing 25,000 metric tons/year of mixed chlorinated hydrocarbon wastes are estimated at $19,700,000/year; the process could produce carbon tetrachloride at 10.2¢ per lb, and the selling price is now 19¢.

V. OUTLOOK FOR WASTES

Chlorinolysis is an efficient, cost-effective process for recovering carbon tetrachloride from chlorinated hydrocarbon waste streams. The outlook for the process depends on the future demand for carbon tetrachloride, and the availability of a continuing supply of suitable wastes.

DIALYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Dialysis is one of the earliest membrane processes. It can separate salts and low molecular weight organics from colloids and high molecular weight solutes in aqueous waste streams. However, both of the output streams are more dilute than the feed stream, and neither is likely to be more suitable for disposal or recovery than the feed stream. Hence, dialysis has little or no potential for general waste treatment applications.

II. PROCESS DESCRIPTION

A solute-containing feed stream is passed across one free of a semi-permeable membrane and a higher volume wash stream is passed across the opposite face. Small solute molecules are transferred to the wash stream by diffusion across the membrane. Larger molecules and colloids are retained in the feed stream.

III. APPLICATIONS TO DATE

The best known current application of dialysis is hemodialysis, which removes salts, urea, and other wastes from the blood of people suffering from chronic kidney failure. Since the 1920's, dialysis has been used in the rayon industry to separate caustic soda from hemicellulose wastes. There are also other smaller scale applications in pharmaceutical and biochemical laboratories for special production and purification. Dialysis equipment is available commercially.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are low, being limited to the pumping of feed and wash streams.

The two diluted product streams could prevent difficult disposal problems if not reusable.

Capital costs depend more on the amount of material to be separated than on the waste stream throughput. A commercial dialyzer separating 1000 lb/day of solute would cost about $3000.

V. OUTLOOK FOR WASTES

Dialysis is a mature technology; no major new developments are expected which would make the process at all useful for hazardous waste treatment.

DISSOLUTION

I. CONCLUSIONS AND RECOMMENDATIONS

Dissolution is a first step that removes major or minor constituents from solids. The process is applicable to any solids that can be wetted by a suitable liquid. We recommend that more emphasis be placed on more complete characterization of solids to aid in specification and testing of possible dissolution processes. Efforts should also be made to utilize lower quality or waste reagents where possible.

II. PROCESS

Dissolution may be defined as the complete or partial transfer of one or more components from a solid to a liquid phase in contact with the solid. The reaction involves some degree of chemical transformation, such as solvation, ionization, or oxidation. The solids are contacted by the reagent in a mixer, following which the slurry is separated. Heat may be applied to speed the process and provide increased solubility. Solids can be treated sequentially with different reagents to remove components selectively. The products are a wastewater stream that requires further treatment, and residual solids that may be suitable for disposal, reuse, or further treatment.

III. APPLICATIONS TO DATE

Dissolution has been widely used in metallurgy since the early 1800's and in the synthetic chemical industry since its beginning. Many of these applications (e.g., separation of metals from ores) are closely related to treatment of inorganic wastes, but there appears to be little large-scale application to waste treatment. One installation involves production of chemicals for agriculture and other use from galvanizing wastes and flue dust. Another is used for recovery of metallic copper from scrap, and a semi-commercial plant is being considered for recovery of metal from plating slimes. Several pilot and laboratories studies are now going on.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are limited to electricity for mixing and pumping, and heat, if required. Emissions to water are not harmful if the liquors used and produced are conveyed to the next process step without inadvertent losses. No land disposal problems are anticipated if leached solids are adequately washed to remove leach liquor. Emissions to air will be significant only when gas is evolved in the process, or where an unintended reaction takes place (e.g., reaction of traces of sulfides in water to give off hydrogen sulfide).

The diversity of materials potentially suitable for dissolution and the circumstances of reaction vary considerably. The process is especially sensitive to chemical and labor costs.

An approximate cost for dissolving a hypothetical metal finishing sludge waste using fresh sulfuric acid reagent would be: $61 per ton of input solids or $300 per ton of desired metal removed; the cost of sulfuric acid is $24 per input ton.

V. OUTLOOK FOR WASTES

Further applications for waste treatment depend on cost-sensitive factors, such as utilization of waste reagents, and on better understanding of composition of sludges and mixed metal compounds.

DISTILLATION

I. CONCLUSIONS AND RECOMMENDATIONS

Distillation is a unit operational process that is fully developed commercially and is often employed to separate or purify liquid organic product streams. It is a non-destructive process, and practical limitations are primarily economic. With more stringent limitations on air, liquid effluents, and land site disposal, and with the rising cost of organic chemicals, distillation could become more competitive with other methods for recovery of useful materials from waste streams.

II. PROCESS

The basic principle of distillation is as simple as it is old: when a mixture of liquids is boiled, the vapor usually differs in composition from the liquid that remains. Only since the 19th century, however, has distillation been conducted on a large scale as a steady-state operation.

In general, a feedstock is charged to a large vessel (still) which is heated, and vapors are removed as they are formed, and then condensed. There are a number of variations on this basic process.

III. APPLICATIONS TO DATE

Distillation has wide industrial application in petroleum fractionation, organic chemical purification, organic chemical intermediate manufacture, solvent recovery, and cryogenic air separation to produce oxygen, nitrogen, and argon.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Because of the variables involved, there is no such thing as a typical cost on a unit product or unit feed basis.

Distillation creates no air or liquid effluent problems.

An economic analysis of a system that might be used for different types of organic liquid waste streams was made, based on a capacity of 8000 lb 20% acetone in water waste/day. The solvent recovery cost in this system would be 4.2¢/lb acetone.

V. OUTLOOK FOR WASTES

Hazardous wastes that can be economically treated by distillation (for organic chemical or solvent recovery) include liquid organic mixtures, such as solvent mixtures recovered from carbon air adsorption units, paint wastes, organic-containing plating wastes, and lube oil. The process is not suitable for treatment of thick, polymeric materials, slurries, sludges, or tars that can cause operational problems. The types and quantities of organic solvent and chemical wastes that are treated by distillation will increase as effluent regulations become more stringent.

ELECTRODIALYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Electrodialysis has not been employed on a full-scale basis for any hazardous waste problem, per se. Nevertheless, it may have applicability where it can be tied into further concentration or reuse schemes. It will profit by the fact that it is a mature technology with well-known performance characteristics and price, and therefore can be easily evaluated as a potential component of any multi-process treatment being considered.

II. PROCESS

The general principle of electrodialysis is the separation of an aqueous stream under the action of an electric field into two streams, one enriched and one depleted. Success depends on synthetic membranes, usually based on ion-exchange resins, which are permeable only to a single-charge type of ion. Cation exchange membranes permit passage of only positive ions, while anion membranes permit only negatively charged ions to pass through.

The feed water passes through compartments formed by the spaces between alternating cation-permeable and anion-permeable membranes held in a stack. At each end of the stack is an electrode having the same area as the membranes. A d-c potential applied across the stack causes the positive and negative ions to migrate in opposite directions. Feed material is first filtered to remove suspended particles that could clog the system. An operating plant usually contains many recirculation, feedback and control loops and pumps to optimize the concentrations and pH at different points for most efficient operation.

III. APPLICATIONS TO DATE

Electrodialysis has been used for desalination since the 1950's. The largest number of installations is in the production of potable water from brackish well or river water. Hundreds of such units, some of which can handle more than one million gallons per day, are in use throughout the world.

In the food industry, electrodialysis is used for desalting whey and de-ashing sugar. The chemical industry uses the technique for enriching or depleting solutions, and for removing mineral constituents from product streams.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Electrical requirements vary, but conventional systems take about 5 kWh of energy for each 1000-ppm reduction of salt in each 1000 gal. purified product water and up to 3 kWh to pump each 1000 gal. products.

The product streams must be recycled, sold, or otherwise disposed of. Electrodialysis may generate low levels of toxic or flammable gases that might present a hazard in an enclosed space.

The capital costs for electrodialysis are modest, about 20-25% of the total cost of water treatment. Both capital and direct operating costs are dependent on the volume of water treated and on the salts removed. Total water production costs of less than \$.50/10^3 gal are reported for salt reduction from 2000 ppm to 500 ppm in plants treating 10^6 gal/day or more. Other plants may have higher costs or may receive significant credits for reclaimed material.

A typical electrodialysis system to treat rinse tanks from an acid nickel plating line might cost about \$6.00/10^3 gal.

V. OUTLOOK FOR WASTES

Pilot operations have been carried out in the desalting of sewage plant effluent, sulfite-liquor recovery, and acid mine drainage treatment. Treatment of plating wastes and rinses, particularly to salvage chromium, may have some potential.

ELECTROLYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Electrolytic processes may be considered for reclaiming heavy metals, including toxic metals from concentrated aqueous solution and for polishing dilute metallic wastewaters. They are not generally useful for dissolved organics, organic waste streams or viscous and tarry liquids.

II. PROCESS

Electrolysis refers to the reactions of oxidation or reduction that take place at the surface of conductive electrodes immersed in an electrolyte, under the influence of an applied potential.

III. APPLICATIONS TO DATE

Electrolysis, including electroplating and anodizing, has been an important process of industrial chemistry for many years. Chlorine production, for example, depends on electrolysis, and many commercial metals are refined by electrolytic processes. Metals may be obtained from primary ores, and magnesium and aluminum are processed by electrolysis in molten salt baths. Electrolysis for waste treatment has been employed to a limited extent depending largely on costs. The most frequent application is the partial removal of concentrated metals such as copper from waste streams for recycle or reuse. Other applications which have been successfully piloted include oxidation of cyanide wastes and separation of oil-water mixtures.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Electrical energy costs range from 10 to 35% of total operating costs, with treatment of concentrated metals at the low end, and dilute streams or cyanide treatment at the high end.

Gaseous emissions may exist: some may be vented to the atmosphere, others may have to be scrubbed or otherwise treated. The process wastewater may be reusable or disposable, or may have to undergo further processing.

Costs are highly dependent on the concentration and nature of the undesirable material. Electrolysis may offer significant trade-offs between capital and operating costs, depending on chemical and economic variables.

ELECTROPHORESIS

I. CONCLUSIONS AND RECOMMENDATIONS

No suitable equipment for electrophoretic treatment of hazardous wastes is available. Many critical problems would have to be solved before such equipment could be developed, and even if the design problems were solved, there is no assurance that the process would be operationally practical. Further consideration of electrophoresis cannot therefore be justified.

II. PROCESS DESCRIPTION

Electrophoresis is the transport of electrically charged particles under the influence of a DC electric field. The charged particles (generally colloids in the 1-20μ size range) migrate to a collecting membrane for subsequent removal.

III. APPLICATIONS TO DATE

Electrophoresis is used extensively as a laboratory tool in the analysis and separation of proteins, polysaccharides, and nucleic acids. It has also been used commercially for creaming of rubber latex, and for fractionation of animal sera for veterinary vaccines. Numerous proposed applications have been researched and shown to be technically feasible. These include deposition of paints, polymers, ceramics, and metals. The process has also been considered for water purification (e.g., for separation of emulsions, and for color, virus, and algae removal).

IV. ENERGY, ENVIRONMENT, ECONOMICS

In aqueous systems, the electrical energy requirements are of the order of 7 kWh/1000 gal.

The process may evolve gases from electrode reactions. Both the concentrated sludge and the "treated" liquid may require subsequent disposal.

Capital costs would be lower than the costs for electrodialysis. Operating costs might be in the range of $0.50-2.00/1000 gal, depending on the application.

V. OUTLOOK FOR WASTES

At least 5-10 years of effort would be required to develop electrophoresis equipment for waste treatment. In view of the lack of scientific and practical guides available, and the very significant problems of controlling electrode reactions, pH, conductivity, flow, temperatures, and membrane plugging, there is even some question whether an R&D effort would be successful.

EVAPORATION

I. CONCLUSIONS AND RECOMMENDATIONS

Evaporation is a well-defined well-established process, used throughout industry. It is capable of handling liquids, slurries, sludges, both organic and inorganic, containing suspended or dissolved solids or dissolved liquids where one of the components is nonvolatile. It is energy-intensive, and specialized equipment can be expensive.

II. PROCESS

The process and equipment for applying heat to the solution are similar to that for distillation, except that the vapor is not separated. Open, direct-fired pans or solar evaporation from ponds are still used in some applications, but most evaporators are heated by steam condensing on metal tubes, through which the solution flows. Usually the steam is at low pressure and the boiling liquid is under a moderate vacuum. There are numerous variations on equipment and processes, depending on the application.

III. APPLICATIONS TO DATE

In the chlor-alkali industry, evaporation is used to concentrate caustic soda and to produce calcium chloride. Evaporation of saline water to provide fresh water is well established; U.S. plants have a capacity of about 67 million gpd. Concentration of sulfuric and hydrochloric acids, citrus fruit juice, phosphates, and milk whey; crystallization of salts, sugar; dehydration of Glaubers salt, sulfur sludges are all well established.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements vary considerably within a range of 100 to 1100 Btu/lb liquid evaporated, with the average closer to the lower figure.

There are generally no pollution problems with evaporation vapors. Where the vapors contain organics, the liquid is condensed and either disposed of or recovered by another process, such as distillation.

Economic analysis of an operation to concentrate 100,000 gallons per hour of kraft black liquor shows capital investment of $1.3 million. Yearly operating costs would be $1.06 per 1000 lbs of water.

V. OUTLOOK FOR WASTES

Evaporation is already used in the treatment of radioactive wastes, and is very effective where suspended solids content is high and other methods are difficult. A combination of evaporation and simultaneous combustion is used to dispose of TNT wastes. Other applications include photographic chemicals, papermill wastes, molasses distillery wastes, and pickling liquors. Evaporation is not suitable for tars, solids, dry powders, or gases.

FILTRATION

I. CONCLUSIONS AND RECOMMENDATIONS

Filtration is a well-developed liquid/solid separation process currently applied to the full-scale treatment of many industrial wastewaters and waste sludges. For the treatment of hazardous wastes, filtration can be used to perform two distinctly different functions:

1) Removal of suspended solids from a liquid (usually aqueous) waste stream with the objective of producing a purified liquid.

2) Increasing the solids concentration, and thereby reducing the volume, of a high concentration liquid/solid mixture (sludge) by removing liquid from the mixture ("sludge dewatering").

As a wastewater treatment process, filtration is usually most applicable when following some form of flocculation and/or sedimentation. As a sludge dewatering process filtration is usually technically and economically competitive with other dewatering processes.

We recommend that filtration be considered as a potentially applicable process for hazardous waste treatment applications requiring the separation of liquid and solid phases.

II. PROCESS

Filtration is a physical process whereby particles suspended in a fluid are separated by forcing the fluid through a porous medium. As the fluid passes through the medium, the suspended particles are trapped on the surface of the medium and/or within the body of the medium. Filter media can be a thick barrier of a granular material, such as sand, coke, coal, or porous ceramic; a thin barrier, such as a filter cloth or screen; a thick barrier composed of a disposable material such as powdered diatomaceous earth or waste ash. The pressure differential to move the fluid through the medium can be induced by gravity, positive pressure, or vacuum. The intended application has a great influence on both the type of filter and its physical features.

III. APPLICATIONS TO DATE

The inorganic chemicals industry employs various forms of filtration to separate precipitated product from waste material. They are commonly used in the manufacture of titanium dioxide, sodium dichromate, aluminum sulfate, and magnesium. The organic chemicals industry also employs filter techniques, e.g., removal of acetylene carbon particles from aqueous quench streams, and removal of dye particles from the reaction bath. Rotary vacuum filters are used to remove impurities in the processing of sugar. Vacuum filtration is often used to remove impurities from lube oils. Boiler feed water and many types of industrial process water have stringent specifications on suspended solids. Filtration is often used in conjunction with precipitation, flocculation, and sedimentation to remove these solids. Filtration is also used as the final step in many industrial wastewater treatment plants.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements for filtration are relatively low. A vacuum filtration system capable of dewatering 36,000 gal/day of sludge containing 6 tons of solids will have a power requirement of only 25 horsepower.

The cost of treatment for both vacuum filtration and press filtration is usually within the range of $20-$45/ton of solids treated (dry basis). For liquid purification the cost of filtration by granular media filters usually varies from $0.10-$0.50 per 1000 gallons of wastewater treated.

V. OUTLOOK FOR WASTES

Major applications are and will be in the removal of suspended solids from wastewater streams and in the volume reduction (dewatering) of waste sludges and slurries. As more and tighter restrictions are placed on wastewater discharge, filtration will often be used after precipitation, flocculation, and sedimentation.

Decreased availability of solid waste disposal sites will further encourage the dewatering of sludges prior to disposal.

Non-aqueous liquids can be subjected to filtration for removal of suspended solids, but highly viscous semi-liquids such as tars are generally not amenable to filtration.

FLOCCULATION, PRECIPITATION, AND SEDIMENTATION

I. CONCLUSIONS AND RECOMMENDATIONS

Flocculation, precipitation, and sedimentation are fully-developed processes currently used in a wide variety of industrial processing and waste treatment applications. While flocculation, precipitation, and sedimentation are individual process steps, they are interrelated, and are often combined into a single overall treatment process. They can be quite readily applied to a variety of aqueous hazardous wastes for the removal of precipitable substances, such as soluble heavy metals and for the removal of solid particles suspended in the liquid. We recommend that these processes be given serious consideration for removal of heavy metals and/or suspended solids from an aqueous waste stream. Although the process theoretically can be used to treat non-aqueous liquids, such applications are very rare. Precipitation, flocculation, and sedimentation are generally unsuitable for treating heavy slurries, sludges, and tars.

II. PROCESS

Flocculation is the process whereby small, unsettleable particles suspended in a liquid are made to agglomerate into larger more settleable particles. Precipitation is a physico-chemical process where some or all of a substance in solution is removed from the solution and transformed into a second (usually solid) phase. Sedimentation is a purely physical process whereby particles suspended in a liquid are made to settle by means of gravitational and inertial forces acting on both the particles suspended in the liquid and the liquid itself.

III. APPLICATIONS TO DATE

The processes have long been widely used for a variety of industrial applications, such as in the manufacture of many organic chemicals, the preparation of metal ores, and the preparation of sugar.

Practically every industry that discharges a process wastewater stream contaminated with suspended and/or precipitable pollutants employs some form of precipitation, flocculation and/or sedimentation. Examples are: removal of heavy metals from iron and steel industry wastewater; removal of fluoride from aluminum production wastewater; removal of heavy metals, from wastewaters from copper smelting and refining, and from the metal finishing industry.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy consumption is very low compared to other processes. The processes produce a waste sludge, which can often present a serious disposal problem.

A large (over 5 million gallons per day) system employing only sedimentation with no flocculating chemicals will typically treat wastewater at a cost of $0.10-$0.50 per 1000 gallons treated.

A moderate size (0.5-5 million gallons per day) system employing precipitation, flocculation, and sedimentation and using moderate dosages of precipitating/flocculating agents will usually treat wastewater at a cost of $0.50-$3.00 per 1000 gallons.

Small, especially designed systems (less than 0.5 million gallons per day) using high dosages of precipitating/flocculating agents can have costs that are higher, but these will rarely exceed $6.00 per 1000 gallons.

V. OUTLOOK FOR WASTES

Precipitation, flocculation, and sedimentation are generally practical, effective, and relatively low-cost processes for the removal of precipitable soluble substances and suspended particles from aqueous waste streams. The processes are particularly suitable for the treatment of high volume/low concentration waste streams.

In determining the applicability of precipitation, flocculation, and sedimentation to specific waste streams, true research and development is usually unnecessary. Past experience and simple laboratory treatability tests are usually all that is necessary in determining applicability.

FLOTATION

I. CONCLUSIONS AND RECOMMENDATIONS

Flotation is a physical-chemical method of separating solid particles suspended in a liquid, when the valuable products to be separated constitute less than 10% of the total solids. Although flotation has found only limited application outside the mineral industry, it is our belief that, with further research and development, the technique could be used to separate many types of components from mixtures of solids.

II. PROCESS DESCRIPTION

The material is crushed or ground, mixed with water and reagents into a slurry or pulp, and agitated. Air bubbles carry the selected materials to the surface to form a stabilized froth, which is then skimmed off, while the waste materials remain. By using the correct reagents, it is possible to separate similar materials from each other. Some installations separate only one valuable component from waste; others separate two, three, or even four products.

III. APPLICATIONS TO DATE

Although flotation has been applied principally to mineral processing to separate valuable ore from tailings, a few other applications seem to have potential. When cellulose is recycled from paper, flotation can be used to remove ink, pigments, and coatings. A few years ago three plants in the United States treated about 25,000 tons of paper per year in this manner.

Other possible applications outside the mineral industry, though there are no commercial plants, are as a means of removing cyanide from solutions or mixed suspensions. In one test, about 95% of the cyanide could be removed. Research also shows that microorganisms can be floated, concentrated, and removed from a suspension.

IV. ENERGY, ENVIRONMENT, ECONOMICS

The typical conventional flotation plant is a relatively large consumer of energy, averaging about 15 kWh/ton milled. Only about 15% of the total is consumed in the flotation step, with most of the energy used for crushing and grinding.

Air emissions are not significant, since flotation is a wet process. Dust emissions occur at the ore crusher and at conveyor transfer points but are controlled with collecting hoods and water sprays. The waste effluent goes to a tailings dam from which water may be recycled, especially in arid areas.

Costs depend on the size and nature of the process. Operating costs for sulfide ore flotations vary from $4/ton ore processed for a 500T/day plant to $1.50/ton for a 10,000 T/day plant.

V. OUTLOOK FOR WASTES

The best application for the flotation process would be for separating a hazardous solid from one that is not. Another application would be to separate all solid materials in a slurry; however, it is difficult to see any reason for doing it this way, when the simpler process of thickening and filtration would accomplish the same purpose. Heavy metal ions (copper, nickel, cadmium) and cyanides might be amenable to removal by this process, as well as such inorganics as carbonyls and fluorides. As far as we know, however, no work has been done to utilize the process.

On the other hand, some of the reagents commonly used for mineral and ore processing are themselves hazardous and, if used carelessly, may appear in the tailings. Care must be exercised in their use and control.

FREEZE-CRYSTALLIZATION

I. CONCLUSIONS AND RECOMMENDATIONS

Freeze-crystallization has been successfully tested for desalination of brackish waters in pilot plants. It has been demonstrated in the laboratory for hazardous waste treatment, and is expected to find commercial applications in the near future.

II. PROCESS DESCRIPTION

Freeze-crystallization involves formation of "pure" ice crystals from a solution, and concentration of dissolved solutes in a residual brine. The ice crystals may be separated mechanically from the brine, washed, and melted to yield fresh water (or solvent). The brine must be treated further, or otherwise disposed of.

III. APPLICATIONS TO DATE

A number of freeze-crystallization processes were developed for desalination, but none have become commercial. Waste treatment applications tested in the laboratory include: sulfite liquors; plating liquors; paper mill bleach solutions; arsenal redwater; solutions containing acetic acid, methanol and aromatic acids; ammonium nitrate wastes; and cooling tower blowdown.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Electrical energy requirements are in the range of about 60-75 kWh/1000 gal of product water.

The major environmental problem is associated with further treatment, or disposal of the brine. Some emissions of refrigerant (e.g., butane or freon) are possible.

Capital costs are estimated to be in the range of $600,000-$800,000. Operating costs might be in the range of $6-12/1000 gal of product water.

V. OUTLOOK FOR WASTES

Freeze-crystallization appears to be a very promising process for treatment of aqueous waste streams containing 1-10% TDS. Commercial applications are certainly anticipated within the next five years. Applications to some non-aqueous waste streams could probably be developed.

FREEZE-DRYING

I. CONCLUSIONS AND RECOMMENDATIONS

Freeze-drying (lyophilization) has no apparent potential for treating hazardous industrial wastes. Although freeze-drying is used commercially for desiccating biological and sensitive materials, it does not appear adaptable to economical waste processing on a large scale. The process is slow, costly, and energy-intensive, with limited use for removing water.

II. PROCESS DESCRIPTION

Freeze-drying is a process for subliming frozen water from a material under high vacuum. Basic equipment consists of a vacuum chamber, a vacuum source, and appropriate refrigeration and heating equipment. Suitable feeds include wet solids, sludges, and slurries.

III. APPLICATIONS TO DATE

The largest current use of this process is in the preparation of freeze-dried coffee which commands a premium price in the marketplace. It is also used in the manufacture of pharmaceutical and biological preparations.

There are no known applications to waste treatment, and none is under development.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Freeze-drying is energy-intensive and costly to operate. Capital equipment costs range from $300,000-500,000. Its pollution potential is low, except for secondary effects of energy generation.

V. OUTLOOK FOR WASTES

Freeze-drying development aimed at waste treatment is unknown and will probably remain so due to the serious limitations of the process.

FREEZING, SUSPENSION

I. CONCLUSIONS AND RECOMMENDATIONS

Freezing of sludges can aid in the agglomeration of suspended particles, which then tend to separate rapidly on thawing, leaving a clean supernatant. There are no practical applications at this time.

II. PROCESS DESCRIPTION

Suspension or simple freezing (dewatering) of sludge causes the suspended solids to agglomerate and form relatively large floc particles which are more easily removed. Freezing is accomplished naturally outdoors or through use of a refrigerant. Flocculants may be used to accelerate coalescence of suspended solids during freezing. Separated solids are screened or filtered off, and the water is further treated if necessary.

III. APPLICATIONS TO DATE

No commercial suspension freezing or freeze dewatering applications exist. Freezing alum sludges typical of waste water treatment plants has been the center of interest in the laboratory. Development of freezing for other materials is not being advanced.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements for natural freezing outdoors are small. Mechanical refrigeration requires large energy expenditures. Suspension freezing is essentially a phase separation process, and both the separated solids and the supernatant liquid would generally require further treatment prior to disposal.

Reliable cost data are not available, but are expected to be relatively high.

V. OUTLOOK FOR WASTES

Unless energy considerations are proven to be acceptable and a broader usage of suspension freezing can be found, it will remain limited in application to sludge dewatering. Its value as a viable waste treatment process remains to be demonstrated on a commercial scale.

HIGH-GRADIENT MAGNETIC SEPARATION (HGMS)

I. CONCLUSIONS AND RECOMMENDATIONS

High-gradient magnetic separation (HGMS) should be considered for removal of magnetic materials, or recovery of certain high-value, nonmagnetic materials, from waste streams. The process is particularly attractive for high-volume applications. Aqueous or non-aqueous liquids, slurries, solids, and dry powders may be treated.

II. PROCESS DESCRIPTION

HGMS is a technique for separating magnet or weakly paramagnetic particles and other nonmagnetic materials (down to colloidal particle size) from slurries, sludges, and (after chemical treatment) from solutions. The feed stream is passed through a fine ferromagnetic filter which, when magnetized, collects the magnetic material. The filter is periodically cleaned, with the magnetic material then recovered by a simple wash procedure. The removal of nonmagnetic material requires the feed to be treated with a magnetic seed (e.g., magnetite).

III. APPLICATIONS TO DATE

Current applications include clay whitening (removal of a small colored magnetic fraction), and upgrading of low-grade iron ore.

Applications currently being investigated, but not yet commercial, include: beneficiation of other ores, coal desulfurization, removal of flue dusts in air streams from blast furnaces, and wastewater treatment (including municipal wastes and steel mill wastewaters).

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements may be relatively large, especially if high magnetic fields are required. Electromagnets, used to generate fields of up to 20 kOe, have power ratings of around 400 kW for the larger machines. Disposal of the filter wash solution, if the material is not recovered, and additional treatment of treated stream may also be required.

Capital costs may be as high as $800,000, if high magnetic fields are required; they may be as low as $5,000, if the material being removed is ferromagnetic. Operating costs for high-volume applications are expected to be around 10-50¢/1000 gal for removal of ferromagnetic materials, and of the order of $1-5/1000 gal for removal of weakly paramagnetic materials.

V. OUTLOOK FOR WASTES

HGMS has attractive possibilities for the removal of ferromagnetic and paramagnetic particulates from liquids or slurries (where seeding is not required). When other nonmagnetic particles are present, the magnetic material should constitute only a small fraction of the total solids; total solids, however, may be as high as 10-15% by volume of the waste stream. Economics are probably favorable only for large-volume streams. The time frame for development is of the order of 5-10 years.

HYDROLYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Hydrolysis is potentially applicable to a wide range of waste forms and compositions. There are currently very few actual waste treatment applications, but the process does appear promising for detoxification and recovery of organics. Expanded R&D activity is recommended.

II. PROCESS DESCRIPTION

Hydrolysis generally refers to double decomposition reactions with water of the type: $XY + H_2O \longrightarrow HY + XOH$. The reactions are usually carried out at elevated temperatures and pressures, often with acid, alkali, or enzyme catalysts. Suitable feed streams include aqueous or non-aqueous solutions, slurries, sludges, or tars.

III. APPLICATIONS TO DATE

The oldest application of hydrolysis is in the production of soap from heated fats in the presence of caustic (known as saponification). Hydrolysis is also used commercially for the manufacture of a variety of organics (e.g., production of phenol from chlorobenzene; production of ethylene oxide from ethylene glycol or ethylene chlorohydrin).

Waste treatment applications are not widespread. However, in the petroleum industry, the sludge from acid treatment of light oils is often hydrolyzed to recover sulfuric acid for reuse; the other product, a tarry acid oil, may be concentrated and burned as fuel. Hydrolysis has also been used for detoxification of waste streams containing carbamates, organophosphorus compounds, and other pesticides.

Hydrolytic waste treatment processes that have shown promise in the laboratory include acid hydrolysis of waste paper to sugar; conversion of organic sludge to animal feed; and decomposition of polyurethane foam to toluene diamine and a polyol.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements vary considerably with the application, but are generally high. Steam requirements for production of fatty acids approximate 120 Btu/lb of product. Production of TiO_2 from $Ti(SO_4)_2$ requires about 1500 Btu steam/lb of TiO_2 produced.

The products of hydrolysis of a complex waste stream are not readily predictable and may be toxic.

The capital investment and operating costs are highly dependent on the specific process details. Capital investment figures for different processes range from about $2500-20,000/ton of material handled daily. Operating costs might range from 0.3-1.5¢/lb.

V. OUTLOOK FOR WASTES

Although not in widespread use as a waste treatment process, hydrolysis presents no fundamental problem. Handling of strong acids and alkalies requires care, and performing reactions at high temperatures and pressures necessitates close control and monitoring.

For hazardous wastes, hydrolysis can be adapted to handle liquids, gases, or solids. It does not appear promising for inorganic materials, but is suitable for a wide range of aliphatic and aromatic organics.

ION EXCHANGE

I. CONCLUSIONS AND RECOMMENDATIONS

Ion exchange is well suited for general and selective removal of heavy metals and toxic anions from dilute aqueous waste streams. The upper concentration limit for efficient operation is about 4000 mg/l. Research on the use of polymer beads impregnated with liquid ion exchange materials has some promise for extending the concentration limits.

II. PROCESS DESCRIPTION

Ion exchange involves the interchange of ions between an aqueous solution and a solid material (the "ion exchanger"). After removal of the solution, the exchanger is then exposed to a second aqueous solution of different composition which removes the ions picked up by the exchanger. The process is most frequently carried out by pumping the solutions through one or more fixed beds of exchanger.

III. APPLICATIONS TO DATE

Full-scale operations include cleanup of dilute solutions from electroplating and other metal-finishing operations, recovery of effluents from fertilizer manufacturing, and industrial deionization. Promising applications include removal of cyanides from mixed streams and use of newer exchangers for selective removal of heavy metals.

IV. ENFRGY, ENVIRONMENT, ECONOMICS

Energy requirements are low, consisting primarily of electricity for pumping solutions.

The dilute purified product stream is dischargeable to sewers. The regenerant stream requires further treatment for recovery or disposal. Minor amounts of exchange materials will require disposal occasionally.

Capital costs are expected to be in the range of $200,000-$350,000, with a substantial investment in resin. Operating costs might be in the vicinity of $2-8/1000 gal.

V. OUTLOOK FOR WASTES

Ion exchange is a well developed process, which promises to be used more widely for recovery of heavy metals, and removal of both heavy metals and cyanides.

LIQUID ION EXCHANGE

I. CONCLUSIONS AND RECOMMENDATIONS

Liquid ion exchange (LIE) is a process with demonstrated potential for removal of heavy metals and hazardous anions from aqueous waste streams. It covers a much wider concentration range than conventional ion exchange. Development of new applications and reagents for waste treatment may require special economic incentives, since historically such research has been stimulated principally by high-volume hydrometallurgical applications.

II. PROCESS DESCRIPTION

Liquid ion exchange involves, first, the extraction of inorganic species (principally ionic) from an aqueous stream into an immiscible organic stream containing special reagents to facilitate the extraction, and then subsequent transfer of the species to a second aqueous stream of different composition from the feed. Process equipment is that commonly used for liquid-liquid extraction: mixer-settlers, differential columns, or centrifugal contactors.

III. APPLICATIONS TO DATE

Full-scale commercial operations include removal of molybdenum and acids from metal pickling baths, zinc from textile production effluents, and copper from various streams. Promising applications include removal of cyanides and treatment of hydroxide slimes from electroplating.

IV. ENERGY, ENVIRONMENT, ECONOMICS

The LIE process has very low energy consumption, consisting principally of electricity for pumping and mixing.

The cleaned feed stream will contain 10-50 mg/l of the organic extraction solvent. The regenerative solution into which hazardous components are stripped from the extraction solvent will require further treatment.

Capital costs depend upon the application. Values in the literature range from $10,000 (almost certainly too low) to $600,000. Total costs for treating dilute streams are estimated to be around $4/1000 gal. For concentrated stream, costs are highly variable, ranging from $0.20-$3.00/lb of metal removed.

V. OUTLOOK FOR WASTES

This method is well-developed, and particularly applicable to recovery of high-value metals from waste streams.

LIQUID-LIQUID EXTRACTION OF ORGANICS

I. CONCLUSIONS AND RECOMMENDATIONS

Liquid-liquid extraction should be considered for the recovery of organic solutes from fairly concentrated aqueous and non-aqueous solutions.

II. PROCESS DESCRIPTION

Liquid-liquid extraction is the separation of the constituents of a liquid solution by contact with another (immiscible) liquid. If the substances comprising the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result. This may be enhanced by the use of multiple contacts. A total recovery process based on liquid-liquid extraction usually requires the use of other unit processes, such as stripping or distillation for solvent and solute recovery.

III. APPLICATIONS TO DATE

Current actual or proven areas of applicability include:

1. Extraction and recovery from aqueous solution of:
    - phenol;
    - acetic acid, and other aliphatic organic acids;
    - salicylic and other hydroxy aromatic acids; and
    - oils.
2. Extraction (without recovery) of:
    - phenol from foul waters near a refinery.
3. Extraction and recovery from organic solvents of:
    - methylene chloride (from isopropyl alcohol);
    - freons (from oils and acetone, or alcohols); and
    - mixed chlorinated hydrocarbons (from acetone or alcohols).

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are usually quite small for just the extraction step. Where solute and solvent recovery require stripping or distillation, steam requirements will be significant.

The only major environmental issues relate to (1) possible need for disposal of recovered solutes if such are not reusable, (2) the probable need for a polishing treatment on the raffinate, following extraction from water, and (3) the possible need for disposal of unwanted fractions following extraction of organic solutions.

Costs cannot be generalized usefully. However, capital investment might be in the vicinity of $1 million. Total operating costs (without credit for resource recovery) might range from well under $1/1000 gal to more than $5/1000 gal.

V. OUTLOOK FOR WASTES

The process is most attractive for treatment of concentrated, selected, and segregated waste streams where material recovery is possible and desirable. Organic solutes, of almost any nature, may be economically removed if concentrations are in the range of a few hundred ppm to a few percent from aqueous waste streams. Organic solutions containing water-soluble and non-water-soluble components may be economically separated by extraction with water.

MICROWAVE DISCHARGE

I. CONCLUSIONS AND RECOMMENDATIONS

Microwave discharge treatment of hazardous wastes is currently in the research stage. Early results are very promising.

II. PROCESS DESCRIPTION

High-frequency microwave power is used to establish a plasma or gaseous discharge in which neutral molecules are partially decomposed into metastable, atomic, free radical and ionic species. The decomposition products typically recombine to form a variety of stable molecules, some of higher molecular weight and of higher toxicity than this feed. Plasmas may be initiated in low-pressure gases of all kinds, and solids and liquids exposed to the reactive species in plasmas generally undergo chemical change. Toxic vapors and liquids introduced into an oxygen plasma undergo reactions similar to those of incineration, but at much lower temperatures.

III. APPLICATIONS TO DATE

Commercial microwave discharge instruments are used in analytical chemistry, particularly for plasma or low-temperature ashing. The only large-scale applications are for photoresist removal and plasma etching in semiconductor device fabrication. Most research has been concentrated on polymer film deposition and organic synthesis. Lockheed is currently investigating the use of microwave plasmas, particularly oxygen plasmas for the treatment of organic vapors and liquids characteristic of waste streams.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Line power requirements for microwave discharge treatment are estimated as roughly 14 kWh/lb of waste treated.

In an oxygen plasma, organic waste components are converted to products similar to those of complete combustion.

Capital costs for a 100 lb/hr facility might be in the neighborhood of $100,000. Operating costs are estimated to be on the order of $1.00/lb.

V. OUTLOOK FOR WASTES

The process should be considered for small quantities of highly toxic materials that cannot be handled by any other means, or for recovery of high-value components.

NEUTRALIZATION

I. CONCLUSIONS AND RECOMMENDATIONS

Neutralization (or more generally pH control) is a technically and economically proven process, currently in full-scale use in many industries. It has wide applicability to waste streams of diverse physical and chemical compositions, and would have to be available in almost any waste treatment facility.

II. PROCESS DESCRIPTION

Neutralization is a liquid-phase chemical reaction between an acid and a base which produces a neutral solution. It may be carried out in batch or continuous flow. It requires reaction tanks, agitators, monitoring and control capability, pumps, and ancillary equipment for handling solids and/or liquids, and storage facilities. The treated stream undergoes no change in physical form, other than solids dissolution (or precipitation) or gas evolution. The process can be used on aqueous and non-aqueous, liquids, slurries, and sludges.

III. APPLICATIONS TO DATE

The process is in full-scale use throughout many industries, e.g., pulp and paper, petroleum refining, and inorganic chemicals. It is used to treat acid exhausts, pickle liquors, plating wastes, and acid mine drainage. It can be used on almost any stream requiring pH adjustment.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are primarily for electricity used to run pumps and stirrers. Treated streams may contain precipitated solids which require additional handling. The solids must be recovered or sent for disposal as a solid waste. There is the possibility of toxic gas being evolved, particularly if sulfides or cyanides are present in the waste stream. Capital investment requirements are highly variable, depending upon the size of the stream to be treated. Operating costs range from $0.20/1000 gal to $4/1000 gal.

V. OUTLOOK FOR WASTES

Neutralization is and will continue to be a routine and accepted part of industrial processing waste management.

OXIDATION, CHEMICAL

I. CONCLUSIONS AND RECOMMENDATIONS

Chemical oxidation and the technology for its large-scale application are well established. Oxidation-reduction, or "Redox" reactions are those in which the oxidation state of at least one reactant is raised while that of another is lowered. We recommend that chemical oxidation be considered for dilute aqueous streams containing hazardous substances or for removing residual traces of contaminants after treatment. Chemical oxidation should be considered as a first treatment step when the waste contains cyanide, when it contains constituents not amenable to other treatment methods, or as a final step to remove traces of contaminants after other treatment.

A more exhaustive study should be made of the potential for treatment of waste containing hazardous materials. Most of the literature deals only with very dilute waste streams, or with the preparation of materials from basic raw materials via chemical oxidative techniques, and little has been published relative to treatment of concentrated hazardous wastes.

II. PROCESS

The first step of the chemical oxidation process is adjustment of the pH of the solution. The oxidizing agent is added gradually and mixed thoroughly. The agent may be in the form of a gas (e.g., chlorine), a liquid (e.g., hydrogen peroxide), or a solid (e.g., potassium permanganate). Because some heat is liberated, concentrated solutions may require cooling, or may require careful measurement and handling to avoid violent reactions.

III. APPLICATIONS TO DATE

,Application to industrial wastes is well developed for cyanides and for phenols, organic sulfur compounds, etc., in dilute waste streams. The primary application has been in converting and destroying cyanides from plating and metal finishing operations.

The chlor-alkali industry uses chemical oxidative techniques to remove mercury from ores, as well as from cell wastes. Mercury removal rates of over 99% are claimed for concentrated ores, and residual mercury levels of less than 0.1 ppm for chlor-alkali sludge.

The technique is also used to remove organic residues from drinking water, or to remove residual chlorine after chlorine treatment. Gases have been treated by scrubbing with oxidizing solutions to destroy odorous substances. Chemical oxidation is also used for odor destruction in the manufacture of kraft paper and in the rendering industry.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Total energy consumption is low; the only requirements are for pumping and mixing.

A disadvantage of chemical oxidation for waste treatment is that it introduces new metal ions into the effluent that might require further treatment. The only waste that appears troublesome is the sludge that can develop in the oxidation treatment of cyanides when iron and some other ions are present. A facility for chemical oxidation of 10^3 gpd of highly concentrated cyanide waste from a plating operation, using batch alkaline chlorination would require a capital investment of \$100,000. Fixed costs would be \$18,300 annually and variable costs \$36,700, giving a unit cost of \$229.20/10^3 gal. For a less highly concentrated waste (100 ppm copper cyanide and 100 ppm sodium cyanide), the operating cost would be about \$170/10^3 gal. Costs could be lowered if the daily flow rate were to increase and the treatment operation could be continuous rather than batch.

V. OUTLOOK FOR WASTES

In addition to the already-established applications for removal of hazardous substances, chemical oxidation may be used to remove chlorinated hydrocarbons and pesticides from dilute streams. Laboratory and pilot studies have demonstrated the potential for this application.

The extent to which the technique can be used to remove hazardous substances from industrial sludges may be limited because of inefficiency and incompleteness of the reaction.

The use of chemical oxidation for concentrated wastes should have careful evaluation for reasons of economics, process safety, and the addition of chemicals that may add to the pollutant load.

OZONATION

I. CONCLUSIONS AND RECOMMENDATIONS

Technology for large-scale ozone application is well developed. Feasibility has been demonstrated for treatment of cyanides and phenols, and laboratory and pilot studies indicate potential for chlorinated hydrocarbons, polynuclear aromatics, and pesticides.

We recommend that ozonation be considered for treatment of aqueous or gaseous waste streams containing less than 1% oxidizable hazardous components and as a preliminary treatment for more concentrated wastes not amenable to other techniques. We also recommend ozonation as a final treatment process where more complete removal of oxidizable substances is required.

A more exhaustive study should be made of the literature on the susceptibility of various compounds to ozonation. Laboratory studies are needed to evaluate the effectiveness of treatment of pollutants of current concern. Additional research and development aimed at more efficient ozone generation and ozone/water mixing should be supported.

II. PROCESS

Since ozone is a powerful oxidizing agent and an extremely reactive gas that cannot be shipped or stored, it must be generated on site immediately prior to use. Ozone generated at a concentration of <2% and a pressure of <15 psi from a stream of air or oxygen previously dried to a dewpoint of -50°C or lower is introduced into a contact chamber designed to ensure good mixing with the waste stream. For aqueous wastes, a venturi injector, a porous diffuser, or an impeller is used to mix ozone and liquid at high velocity for 10 minutes or more. Liquid depth is at least 15 feet, and two or more reactors are frequently employed. For gaseous waste streams, a porous diffuser is used if ozonized air is generated at positive pressure; at atmospheric pressure, a wet scrubbing process is used, with a fine mist of ozone-saturated water sprayed into a contact chamber. Contact times for gaseous streams is 5-60 seconds.

III. APPLICATIONS TO DATE

Ozone, besides being a powerful reducing agent, has antibacterial and antiviral properties. This disinfecting power has been responsible for most large-scale applications. The process is widely used in Europe to purify and improve drinking water, and there have been a number of installations in the United States for treatment of municipal sewage plant effluents. It has also been used to remove sulfide and other odors from rendering plant effluent; fermentation odors from a pharmaceutical plant; treatment of liquid effluent containing cyanides, sulfides, sulfites and other hazardous components after biological treatment; reduce cyanide levels from effluent of a tire plant, a chemical plant, and an electroplating facility. In combination with activated carbon adsorption, ozonation has been used to remove color from waste dyeing water. Oxidation of phenols in coke oven wastes, wood products waste and biologically treated refinery waste.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Ozonation can be expensive, but may be economically competitive for treatment of dilute waste streams. Generation of ozone is the dominant cost component in terms of capital and power. With air feed, energy requirements are from 7.2 to 9.0 kWh/lb of ozone generated. Power requirements are half this figure if oxygen is used for feed. Any improvement in ozone demand or efficiency would improve economics; the catalytic effect of UV light can extend the effect of ozonation dramatically and can reduce ozone demand by a factor of two. Labor and space requirements are low.

Concentrations of ozone leaving the contact chamber are carefully monitored; sometimes the ozonized air is cycled to provide pretreatment of incoming aqueous waste. The waste stream effluent is also monitored, and the dosage increased if necessary. Gaseous effluent is discharged directly to the atmosphere; aqueous effluent may be discharged to a sewer or natural body of water where the oxygen-rich water is beneficial.

V. OUTLOOK FOR WASTES

Complete oxidation to CO_2 can sometimes be achieved; in other cases, oxidized intermediates may be formed that resist further ozonation. Whether a given degree of oxidation constitutes satisfactory treatment depends on the criteria for the particular waste stream or disposal site. Slurries, tars, sludges and solutions in oxidizable liquids are generally not suitable for ozonation. Although ozone itself is a toxic substance, the risk of exposure to toxic levels is small.

PHOTOLYSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Technology for large-scale application of photolysis to wastes is not highly developed. Further laboratory studies of photolysis of selected candidate waste streams (for example, pesticide contaminated solvents) should be conducted. Pure photolysis is not likely to be a practical industrial waste treatment process within the next 5-10 years, but UV-assisted ozonation and chlorination are promising in the near term.

II. PROCESS DESCRIPTION

In photolysis, chemical bonds are broken under the influence of UV or visible light. Products of photodegradation vary according to the matrix in which the process occurs, but the complete conversion of an organic contaminant to CO_2, H_2O, etc., is not probable. Equipment required includes a source of UV/visible radiation, such as a mercury arc. Reactor geometry and materials of construction must allow adequate penetration of the light into the waste.

III. APPLICATIONS TO DATE

Pure photolysis has been investigated only in laboratory-scale studies. Combined UV/ozonolysis and UV/chlorination have been used in pilot and full-scale applications in the hazardous waste area.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Any photolysis process is relatively energy-intensive. There are not sufficient data to allow estimation of either process economics or environmental issues. In general, the process effluent is a stream with physical characteristics similar to those of the input stream, but with different chemical characteristics. Organic hazardous components are not completely degraded and the residues may still pose hazard.

V. OUTLOOK FOR WASTES

Applications are probably highly specialized, detoxification of pesticide-contaminated solvents is one possibility. However, pure photolysis requires research and testing at laboratory and pilot-scale to demonstrate applicability to hazardous waste.

REDUCTION, CHEMICAL

I. CONCLUSIONS AND RECOMMENDATIONS

Reduction reactions are among the most common chemical processes. reduction-oxidation or "Redox" reactions are those in which the oxidation state of at least one substance is raised while another is lowered. The technology for large-scale reduction of some industrial wastes, sometimes allowing recovery of metals, is well developed. We believe that the process could well be adapted to remove hazardous substances from dilute wastes, to pretreat wastes that have constituents not amenable to other methods, and to remove traces of contaminants.

II. PROCESS

The equipment for reduction processes is simple: only storage, metering, mixing, pumping and instrumentation, with the major cost for reducing chemicals. The economics vary with the substance being treated. Introduction of foreign ions into the stream is a real or potential disadvantage; otherwise it is straightforward.

III. APPLICATIONS TO DATE

The application to industrial wastes is already well established for dilute waste streams, especially those containing chromium (VI), and other hazardous substances, such as lead and mercury. In addition to detoxifying hazardous substances, the process sometimes allows recovery of metals. The plating and tanning industries use the process to reduce highly toxic chromium (VI), to chromium (III), which is less hazardous and can be precipitated for removal.

The process also finds application in the chlor-alkali industry for removal of mercury from effluents. It appears to have potential for removing other hazardous substances, e.g., cadmium and antimony, in diluted streams.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Total energy consumption is low; the only requirements are for pumping and mixing.

A disadvantage of chemical reduction for waste treatment is that it may introduce new ions into the effluent that might necessitate further treatment. Air emissions are not significant. There may be problems with land disposal or residues, especially those susceptible to acid leaking. A facility for chemical reduction of 2,000 gpd of chromium (VI) waste from a plating operating, using batch sulfur dioxide treatment would require a capital investment of \$230,000. Variable operating costs would be \$51,400 and fixed costs \$41,600 annually. Unit costs would be \$193.80/10^3 gal. Costs could be lowered if the daily flow rate were to increase and the treatment operation could be continuous rather than batch.

V. OUTLOOK FOR WASTES

We believe there should be a more exhaustive study of the potential for reduction processes for concentrated hazardous wastes. It should certainly be considered as a treatment step whenever chromium VI is a constituent of the effluent. It may be a method for treating wastes that have constituents not amenable to other treatment, and as a final polishing step for removing traces of contaminants.

REVERSE OSMOSIS

I. CONCLUSIONS AND RECOMMENDATIONS

Reverse osmosis (RO) should be considered for treatment of aqueous waste streams containing organic and inorganic species in solution. Total dissolved solids in the feed stream may be as high as 34,000 ppm.

II. PROCESS DESCRIPTION

The heart of the reverse osmosis process is a semipermeable membrane which is permeable to solvent, but impermeable to most dissolved species, both organic and inorganic. Separation is brought about by means of an applied pressure gradient. To protect the membranes for chemical attack and plugging, oxidants, iron and manganese salts, and oils and greases are generally removed prior to application of RO.

III. APPLICATIONS TO DATE

There are about 300 full-scale plants worldwide using reverse osmosis for desalination of sea or brackish water. Reverse osmosis has been used very successfully in the treatment of electroplating rinse waters, not only to meet effluent discharge standards, but also to recover concentrated metal solutions for reuse. A limited number of other full-scale uses can be found in the treatment of sulfite streams from the paper industry and in food processing.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Energy requirements are of the order of 10 kWh/1000 gal of product water.

The concentrated brine or solute solution presents a problem for disposal, if not recoverable.

Capital costs range from about $0.50-4/gpd of purified water output, depending on the volume of waste to be treated. Total operating costs are in the range of $1-5/1000 gal.

V. OUTLOOK FOR WASTES

Use of RO for industrial waste treatment is growing rapidly. The process is particularly useful for concentrating waste streams containing dissolved organics or inorganics, to facilitate recovery, or to reduce volume.

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STEAM DISTILLATION

I. CONCLUSIONS AND RECOMMENDATIONS

Steam distillation is a proven process for removing water-immiscible, volatile compounds from process or waste streams. It can be applied to any stream that can be contacted with steam or water without reaction or decomposition. It can be used with liquids, slurries, sludges, and solids.

II. PROCESS

Steam distillation takes advantage of the unique vapor pressure relationship of two immiscible liquids. The additive vapor pressures allow distillation at lower temperatures. It is usually conducted as a batch operation: the still is charged, the charge is heated to temperature, and the distillation conducted by bubbling steam through the liquid phase. In semi-batch operation, the charge containing a high ratio of volatiles to non-volatiles is fed to the still continuously for a given period while the volatile component is steam-distilled from the mixture.

III. APPLICATIONS TO DATE

The widest application is in the petroleum industry where steam and feedstock are introduced into a multi-tray distillation column to produce gasoline, lube oil, or naphtha. Without the use of steam or steam and vacuum together, the high distillation temperature would result in decomposition. The process is also used for removing low boiling components from a mixture. In the soap industry, glycerine is recovered from spent soap lye; in the naval stores industry turpentine and gum rosin are recovered from pine gum; fatty acids and tall oil rosin are obtained from crude tall oil, a by-product of sulfate wood pulp production. A solvent extraction process removes organics from paper before the wood fiber can be reused; through steam distillation the solvent is recovered. In the production of coke from coal, quantities of aromatic hydrocarbons are also produced. The wash oils from the ovens are steam stripped to recover the aromatic hydrocarbons.

IV. ENERGY, ENVIRONMENT, ECONOMICS

The major energy requirement is for steam. In one application, the steam requirement would total 29,200 lb per 3,000 gal of treated degreasing waste, or per 1,000 gal recovered perchlorethylene. Power requirements would be 30 kWh per 3,000 gal waste.

The wastewater from condensed steam in the steam distillation process will contain traces of volatile organics, and may have to be steam-stripped before disposal.

The fixed capital investment (new equipment) for a steam distillation unit with a capacity of 3,000 gal/week degreasing solvent would be about $130,000. Operating costs would be $1,424. Credits for perchlorethylene at $2/gal and $0.05/gal for the oil/grease mixture used for boiler fuel would more than offset treatment cost.

V. OUTLOOK FOR WASTES

Numerous industrial wastes are treated by contract disposal companies using steam distillation to recover valuable components or reduce waste volumes. With the increase in value of hydrocarbon solvents and increasingly strict regulations regarding landfill with sludges containing these solvents, the use of steam distillation is expected to increase.

STRIPPING, AIR

I. CONCLUSIONS AND RECOMMENDATIONS

Air stripping of ammonia from biologically treated domestic wastewater is being developed as a means of reducing nitrogen content before discharge. It is suitable only for dilute solutions, since the emission level of ammonia from a concentrated solution would be too high. Furthermore, steam stripping would permit recovery of the ammonia from more concentrated solutions. Application of air stripping to other gaseous compounds would depend on the environmental impact of the resulting emissions.

II. PROCESS

Holding ponds, with or without surface agitation, and spray ponds have been investigated, but the packed tower appears to be the most compact and efficient means of air stripping. Removal efficiencies of over 90% have been obtained in pilot tests with wastewater containing 60 ppm nitrogen. The wastewater containing ammonia and a lime slurry (lime added for phosphate removal) are fed to a rapid mix tank, and thence to a settling basin, where the calcium phosphate and calcium carbonate settle out. The clarified wastewater is pumped to the top of two towers packed with a series of horizontal pipes. Air is drawn up through the tower against the falling wastewater by large fans. After the ammonia is removed, the wastewater flows into the recarbonation basin where compressed carbon dioxide-rich gas from the lime recalcining furnace is bubbled through to precipitate and recover calcium carbonate, for calcination and recycle of lime to the system.

III. APPLICATIONS TO DATE

Full-scale packed towers have been used at two locations in California for treating domestic wastewater.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Electric power requirements for treating 15 million gpd are in the range from 1600 to 1800 kWh/hr. The recalciner requires about 8 million Btu (8000 ft^3) natural gas/ton of feed, or 192 million Btu/day.

When the ammonia concentration is about 23 ppm and the air-to-water ratio is 500 ft^3/gal, the concentrated ammonia in the saturated air leaving the tower is about 6 mg/m^3, well below the odor threshold. Disposal of about 25 tons/day of sludge requires a significant amount of land, but does not pose an environmental hazard.

The capital investment would be about $7.8 million; fixed costs would be $1,420,000, and variable operating costs would be $940,000/year.

V. OUTLOOK FOR WASTES

It is unlikely that many other applications of air stripping will be found.

STRIPPING, STEAM

I. CONCLUSIONS AND RECOMMENDATIONS

Steam stripping should be considered whenever it is desirable to remove volatile components (e.g., organics, H_2S, NH_3) from aqueous waste streams.

II. PROCESS DESCRIPTION

Steam stripping may be considered a form of fractional distillation. Live steam is injected into the bottom of the distillation column, and carries dilute volatile components with it. There are two aqueous output streams, one a concentrated solution of the volatile organics and the other a dilute stream containing only residual traces of volatile organics.

III. APPLICATIONS TO DATE

Steam stripping has been used for many years to recover ammonia from coke oven gas. It is also used to recover sulfur as H_2S from refinery raw waste. Other applications include phenol recovery, vinyl chloride monomer removal from PVC suspension resins, and removal of organics and sulfur from Kraft mill condensates. Research work is in progress for steam stripping of light chlorinated hydrocarbons from industrial waste water.

IV. ENERGY, ENVIRONMENT, ECONOMICS

The primary energy requirements are for steam. Between 0.5 and 2.5 pounds of steam are required per gallon of waste water. The concentrated stream containing the bulk of the volatile organic components is processed for recovery or incinerated. If the incinerated stream contains sulfur, emission of SO_2 must be considered. The impact of discharging the treated dilute stream depends on the nature and residual concentration of the volatile organics of the waste water.

Capital investment for a new 200-gpm, single-stage (one column) "sour water" steam stripper would be between $500,000 for mild steel and $850,000 for stainless-steel construction. Treatment cost by this system would be about $10/1000 gal. A capital investment closer to $1,700,000, would be required for a two-stage, two-column, 200-gpm system that would recover NH_3 and H_2S for credits.

V. OUTLOOK FOR WASTES

The use of steam stripping for industrial waste treatment is growing. The most attractive applications are those that permit byproduct recovery, thus to offset fairly high operating costs. The process is energy-intensive, with steam costs amounting to close to 80% of operating costs.

ULTRAFILTRATION

I. CONCLUSIONS AND RECOMMENDATIONS

Ultrafiltration is a membrane filtration process that separates high molecular weight solutes or colloids from their surrounding media. The process has been successfully applied to both homogeneous solutions and to colloidal suspensions that are difficult to separate by other techniques. Commercial use has been focused on aqueous solutions.

Retained solute or particle size is one characteristic distinguishing ultrafiltration from other filtration processes. It filters out particles as small as 10^{-3} to 10^{-2} microns. Where solutes are being separated from solution, the process can serve as a concentration or fractionation process for single-phase streams. It competes with adsorptive and evaporative processes, and has the potential for broader applicability than conventional filtration. Usually the concentrate requires further processing if a pure solute is to be recovered.

II. PROCESS

Ultrafiltration membranes have an extremely thin selective layer supported on a thicker spongy substructure, and it is possible to tailor membranes with a wide range of selective properties. A solution containing molecules too small to be retained by the membrane and larger molecules that will be 100% retained is passed in a pressurized stream. The larger molecules are collected from the upstream side and the smaller molecules downstream.

III. APPLICATIONS TO DATE

Ultrafiltration is used for electrocoat paint rejuvenation and rinse water recovery, protein recovery from cheese whey, and metal machining oil emulsion treatment, with capacity to handle approximately 100 million gallons per year for each application. There are also smaller (on the order of 10 million gpy) plants for treatment of textile sizing waste and wash water from electronics component manufacturing, and for production of sterile water for pharmaceutical manufacturing.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Electrical energy for pumping to maintain flow at operating pressures may be as much as 30% of total direct operating costs.

Ultrafiltration residues are typically a concentrate of the undesirable or hazardous components and usually require further processing unless valuable by-products can be recovered.

Capital and operating costs are dependent on the specific application and the capacity of the system. For large plants, capital costs may be \$1-\$4/gpd; operating costs may be \$5-\$10 per 10^3 gal. Coupled with the economies of reuse of salvaged materials, these costs are often acceptable.

V. OUTLOOK FOR WASTES

There are a number of other applications where ultrafiltration may become commercial within the next five years. These include: treatment of dye waste, pulp-mill waste, industrial laundry waste, and recovery of sugar from orange-juice pulp, protein from soy whey, products from pharmaceutical and fermentation industries, and purification of power-plant boiler feedwater and water for beverages.

Application to hazardous wastes is already well advanced, since many of the aqueous solutions treated present severe sewage problems.

ZONE REFINING

I. CONCLUSIONS AND RECOMMENDATIONS

Zone refining is unlikely to be useful for treatment of hazardous wastes. Although zone refining is an effective purification technique, it has inherent limitations which make its use for broad treatment of large quantities of waste unlikely in the near future. Zone refining is a slow and costly operation, energy-intensive, and, at present, suitable for operation up to only about 10 kg batches.

II. PROCESS DESCRIPTION

Zone refining is a fractional crystallization technique in which a rod of impure material is purified by heating it so as to cause a molten zone to pass along its length. Basic equipment consists of a material support or ingot holder to contain the sample; a feed or travel mechanism; and a source of heat. The process may include a cooling step. It can be used on solids, liquids, and mixtures such as slurries. High viscosity and reactive materials are not suitable.

III. APPLICATIONS TO DATE

Zone refining is used to purify elements, metals, semiconductor materials, oxides, salts, and organic materials in the laboratory. Its primary commercial use is in purification of semiconductor materials.

It is used on relatively pure materials. It is not now used for hazardous wastes, and there are no known proposed applications for hazardous waste.

IV. ENERGY, ENVIRONMENT, ECONOMICS

Zone refining is an energy-intensive process and therefore expensive to operate.

Its pollution potential is low. Equipment costs are not presently available, most equipment being engineered on a custom basis.

V. OUTLOOK FOR WASTES

Zone refining, at present, is only useful for processing small quantities (up to 10 kg) of relatively pure material. Processing rates are under 10 cm/hr. The process is not practical for the complex mixtures that characterize most waste streams. Even for specialized applications, the process is only operationally feasible if the distribution coefficients permit segregation of impurities.

PART TWO

TREATMENT TECHNIQUES

ADSORPTION, CARBON

Prepared by:

Warren J. Lyman

I. CONCLUSIONS AND RECOMMENDATIONS

Carbon adsorption systems have been demonstrated to be practical and economical: (1) for the reduction of COD, BOD and related parameters in secondary municipal and industrial wastewaters ("tertiary treatment"); (2) for the reduction of COD, BOD and related parameters in primary municipal and industrial wastewaters ("physical-chemical treatment"); (3) for the removal of toxic or refractory organics from isolated industrial wastewaters; (4) for the removal *and recovery* of certain organics from wastewaters, and (5) for the removal, at times with recovery, of select inorganic chemicals from aqueous wastes.

The technology for systems employing adsorption of organics followed by the thermal reactivation of the carbon (which destroys the adsorbates) is relatively well developed. Systems employing chemical regeneration, with recovery of adsorbates, are less developed; the potential for carbon systems in such applications (i.e., for the recovery of both organic and inorganic chemicals) is greater than is generally realized.

Waste treatment applications to non-aqueous wastes are not, to our knowledge, being developed but may be possible since decolorization of organic product streams with carbon is common in industry. Vapor-phase applications of carbon are well developed and in wide use in industry but this application is not covered in this report.

Carbon adsorption systems, especially those employing thermal regeneration, are generally considered to involve both high capital and operating costs. The process economies achievable with thermal reactivation of the carbon (on site) may only be realized if carbon usage is above 1000 lbs/day; if wastewater flows are above 10-50,000 gpd, and the adsorbate concentrations are not too low, then thermal reactivation will probably be economical. Below these cut-off points it is more economical to purchase new carbon or to use the services of a centralized reactivation facility.

Carbon adsorption should thus be given serious consideration when it is desirable to remove mixed organics from wastewaters, to remove select inorganics from wastewaters, or to recover select organic or inorganic species from aqueous solution. The concentration of adsorbates in the influent should be less than 1% when recovery is not involved; concentrations up to 5% are acceptable when recovery is involved.

II. PROCESS DESCRIPTION

A. BACKGROUND

Adsorption on activated carbon, while considered advanced waste treatment in certain areas, has a long history (see Ref. 1). Some medicinal properties of charcoal were known over 3,500 years ago, and the decolorization and gas adsorption properties of various chars were first investigated in the late 19th Century. Commercial activated carbons first appeared in the early part of the 20th Century and their development was given a large push by applications in the sugar industry (decolorization) and by the need to develop gas adsorbents to protect against the poison gases used in World War I.

The publicity and interest generated by the development of carbon filters in gas masks led to a search for other applications. Carbons for decolorization and the purification of drinking water supplies grew in use, resulting in a U.S. production of 76 million pounds of activated carbon by 1950 for such uses (Ref. 2). In the last five years, U.S. production of activated carbon has been in the range of 150-200 million pounds per year; nearly half of this is believed to be granular carbon; the remainder is powdered carbon (Ref. 2).

The use of activated carbons for the treatment of liquid waste is, however, a relatively recent phenomenon. The first large-scale system in the United States was the unit designed to give tertiary treatment of the 7.5 MGD of municipal wastewaters at South Lake Tahoe in California; operations started in March 1968, and continue today with satisfactory results. Industrial wastewater treatment with activated carbon dates from about 1969.

B. UNDERLYING PRINCIPLES

The term activated carbon applies to any amorphous form of carbon that has been specially treated to give high adsorption capacities. Typical raw materials include coal, wood, coconut shells, pulp mill residues, petroleum base residues, and char from sewage sludge pyrolysis. A carefully controlled process of dehydration, carbonization, and oxidation yields a product which, while not pure carbon, is called activated carbon. This material has a high capacity for adsorption due primarily to the large surface area available for adsorption, 500-1500 square meters/gram, resulting from a large number of internal pores. Pore sizes generally range from 10-100 Angstroms in radius. Most of the available surface area is non-polar in nature, but the interaction with oxygen (in production) does produce specific active sites which give the surface a slightly polar nature.

Adsorption on activated carbon occurs when a molecule is brought up to its surface and held there by physical and/or chemical forces. This process is reversible, thus allowing activated carbons to be regenerated (and reused) by the proper application of heat and steam, or solvent. (More detailed descriptions on the principles underlying carbon adsorption are given in Refs. 1 and 3.)

After initially contacting an activated carbon with a solution, an equilibrium will eventually be reached such that the rates of solute adsorption and desorption are equal. The amount of solute adsorbed per unit weight of carbon will increase as the concentration of the solute in the solution is increased. In general, adsorption equilibria are governed by two types of interactions: solute-adsorbent and solute-solvent. Thus, the forces favoring dissolution and the forces favoring adsorption are in competition; any change in a system which tends to decrease the dissolution forces or increases the adsorption forces will shift the equilibrium towards higher adsorption per unit weight of carbon.

Some important, but general, rules resulting from considerations relating to the above factors are given below:

- Higher surface areas will give a greater adsorption capacity.
- Larger pore sizes will give a greater adsorption capacity for large molecules.
- Adsorptivity will increase as the solubility of the solute (in the solvent) decreases. Thus, for hydrocarbons, adsorption increases with molecular weight.
- For solutes with ionizable groups, maximum adsorption will be achieved at a pH corresponding to the minimum ionization.
- Adsorption capacity will decrease with increasing temperature (since adsorption is an exothermic process). In practice, this effect is generally small.

The above factors all related to adsorption capacity; the rate of adsorption is also an important consideration. For example, while capacity is increased with the adsorption of higher molecular weight hydrocarbons, the rate of adsorption is decreased. Similarly, while temperature increases will decrease the capacity it may – depending on the rate limiting step in the overall process – increase the rate of removal of solute from solution.

One additional point to remember is that biological activity will usually take place in a carbon bed; if (1) the concentration of adsorbed species is high enough, and (2) the material is biodegradable and non-toxic to the bacteria, then biological degradation may significantly increase the effective removal capacity. Biological activity usually becomes important after many hours of operation. During this time the bacteria have become acclimated and the colony has grown to a significant concentration. In some cases the absorptive life of the activated carbon is doubled.

C. OPERATING CHARACTERISTICS

1. Feed Streams

a. Waste Forms That Can Be Treated

In general, carbon adsorption is applicable only to single-phase fluid waste streams, e.g., liquid solutions or gas mixtures.* In actual applications, both aqueous and non-aqueous liquids are treated with carbon. The non-aqueous streams include petroleum fractions, syrups, animal and vegetable oils, and pharmaceutical preparations; color removal is the most common application in such cases. Current waste treatment applications are limited to aqueous solutions.

Suspended solids in the influent (which lead to premature pressure drops in a carbon bed) should generally be less than 50 ppm to minimize backwash requirements; a downflow carbon bed can handle much higher levels (up to 2000 ppm), but frequent backwashings would be required. Backwashing more than two or three times a day is not desirable; at 50 ppm suspended solids, one backwash per day will often suffice. In any upflow packed bed excessive suspended solids can lead to clogging. Oil and grease should be less than about 10 ppm. A high level of dissolved inorganic material in the influent may cause problems with thermal carbon reactivation (i.e., scaling and serious loss of activity) unless appropriate preventive steps are taken; such steps might include pH control, softening, or the use of an acid wash on the carbon prior to reactivation.

Technically, there are no limits on the concentration of the solute(s) in the feed stream, but in practice about the highest concentration influent that has been treated on a continuous basis contained about 10,000 ppm TOC. One important factor concerning concentration must be kept in mind; since the slopes of adsorption isotherms are almost always positive, the weight percent pickup (solute on carbon) will be higher for the more concentrated influent leading to more efficient solute removal. Additionally, if the carbon is to be regenerated after use, then higher concentration influents may also involve less frequent regeneration, especially if the slope of the adsorption isotherm is greater than 1. When using carbon adsorption to clean up an industrial waste stream the controlling parameter is the quality of the effluent. Concentration of toxic materials in the feed must be balanced against feed rate, and the activity of the carbon to attain effluent quality.

There are no technical limits on the flow rate of the feed stream. The main consideration is cost. Carbon adsorption will benefit significantly from the economics of scale, especially the thermal reactivation portion. If carbon usage is less than roughly 1,000 lbs/day, it may be cheaper to dispose of the carbon than to reactivate it thermally on site. The real economies of carbon adsorption with on-site thermal reactivation will not be realized until carbon usage is above about 8,000 lbs/day. Using the lower figure 1,000 lbs/day and, as an example, an industrial effluent (e.g., effluent from a biological treatment system) that required the use of 5 lbs of carbon/1000 gallons of wastewater, the indicated flow is 200,000 gallons/day. This example should not be considered a cut-off point; in practice, industrial waste streams with flows in the range of 10,000 to 40,000 gallons/day have been successfully treated with carbon adsorption systems incorporating thermal reactivation. For lower flows, there are three options: (1) disposal (i.e., incineration or land fill) of the carbon after use, or (2) storage of the used carbon until an adequate amount is available to send to a central carbon reactivation service center,* or (3) non-thermal regeneration (e.g., with acid, base or solvent).

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*Gas-phase and vapor-phase applications of carbon adsorption, while important, are not covered in this report.

b. Chemicals That May Be Removed

A wide variety of organic and inorganic solutes may be efficiently adsorbed on activated carbon. Applications involving organic solutes are more prevalent and will be most attractive when the solutes have a high molecular weight, low water solubility, low polarity, and low degree of ionization. (Some examples of actual applications are given in Tables 7 through 12 in Section VI of this report.) Highly water soluble organics which often contain two or more hydrophylic groups are difficult to remove. For example, the adsorption of glycols from an industrial waste stream was found to be unfeasible in one recent study due to the low capacity of the carbon for the glycols (Ref. 4). In another case, the treatment of wastewaters from a polyvinyl chloride production plant was found to be impractical; poor adsorption characteristics were attributed to the presence of long-chain organic soaps contained in the wastes (Ref. 5). For some examples low adsorption efficiency, e.g., acetic acid adsorption, the higher process costs may be off-set by solute recovery. Macromolecules, including certain dyes, may be too large to reach a significant fraction of the carbon's internal pores and therefore difficult to remove. Most industrial waste streams contain multiple impurities, some of which are easily adsorbed on carbon, while others are not. In considering the use of an activated carbon system a series of laboratory tests is mandatory. Such tests should include both equilibrium adsorption isotherms and carbon column studies.

Carbon adsorption of inorganic compounds, e.g., the removal of cyanide (Ref. 6) and chromium (Ref. 7) from electroplating wastes has been found to be practical. Other sources (Refs. 1, 8-10) indicate that a wide variety of other inorganics will adsorb on activated carbon. However, adsorption may be quite variable from chemical to chemical, is likely to be highly pH dependent, and thermal or chemical regeneration may not be feasible. In general, strong electrolytes will not be adsorbed on carbon. A summary of some of the inorganic species that may be removed by carbon is given in Table 1. Removal of inorganic solutes by carbon will generally involve influent concentration of less than 1,000 ppm preferably less than 500 ppm. Processes other than physical or chemical adsorption may be involved. Plating may occur in some cases (e.g., with ferric salts) and chemical reactions in others (e.g., reduction of ammonia to chloramines followed by adsorption of the chloramines).

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*Two centers are currently operated by Calgon Corporation, Pittsburgh, Pennsylvania.

TABLE 1
SOME INORGANIC CHEMICALS WHICH MAY BE REMOVED BY ACTIVATED CARBON

Iodine
Chlorine
Gold chloride
Permanganates
Dichromates
Mercuric chloride
Molybdates
Ferric salts
Arsenates
Silver salts
Chromium
Cyanide
Copper
Lead
Selenium
Zinc
Alkali metals (from basic solutions)
Cobalt
Calcium hypochlorite
Sodium hypochlorite
Hypochlorous acid
Hydrogen sulfide
Ammonia

Source: Refs. 1, 6-10

2. How Process Operates

a. Overview

The process of carbon adsorption involves two basic steps as shown in Figure 1. First, the waste stream is contacted with the carbon which selectively adsorbs the hazardous material and allows the purified stream to pass through. Second, when the carbon reaches its maximum capacity for adsorption (or when the effluent is unacceptable for discharge, i.e., when a breakthrough of hazardous material occurs), it must be removed for disposal, destruction, or regeneration. If a breakthrough of impurities occurs long before the full absorptive capacity is reached, then either the rate of feed is reduced or the carbon is replaced. In some cases, carbon can be regenerated in such a way that adsorbed material is recovered.

b. Granular versus Powdered Activated Carbon

Activated carbon is available in both powdered and granular form. Powdered carbon is less expensive and may have a slighly higher adsorption capacity, but it suffers from four drawbacks: (1) it is difficult to regenerate (without high losses); (2) it is more difficult to handle (the settling characteristics may be poor); (3) in the presence of suspended solids coagulation may occur (since powdered carbon is a good coagulant); and (4) larger amounts (on a lb/1000 gal basis) may be required than for granular systems in order to obtain good contact. There are, at present, no fullscale applications of industrial waste treatment incorporating powdered carbon and, thus, further discussion in this report will assume the use of granular carbon.

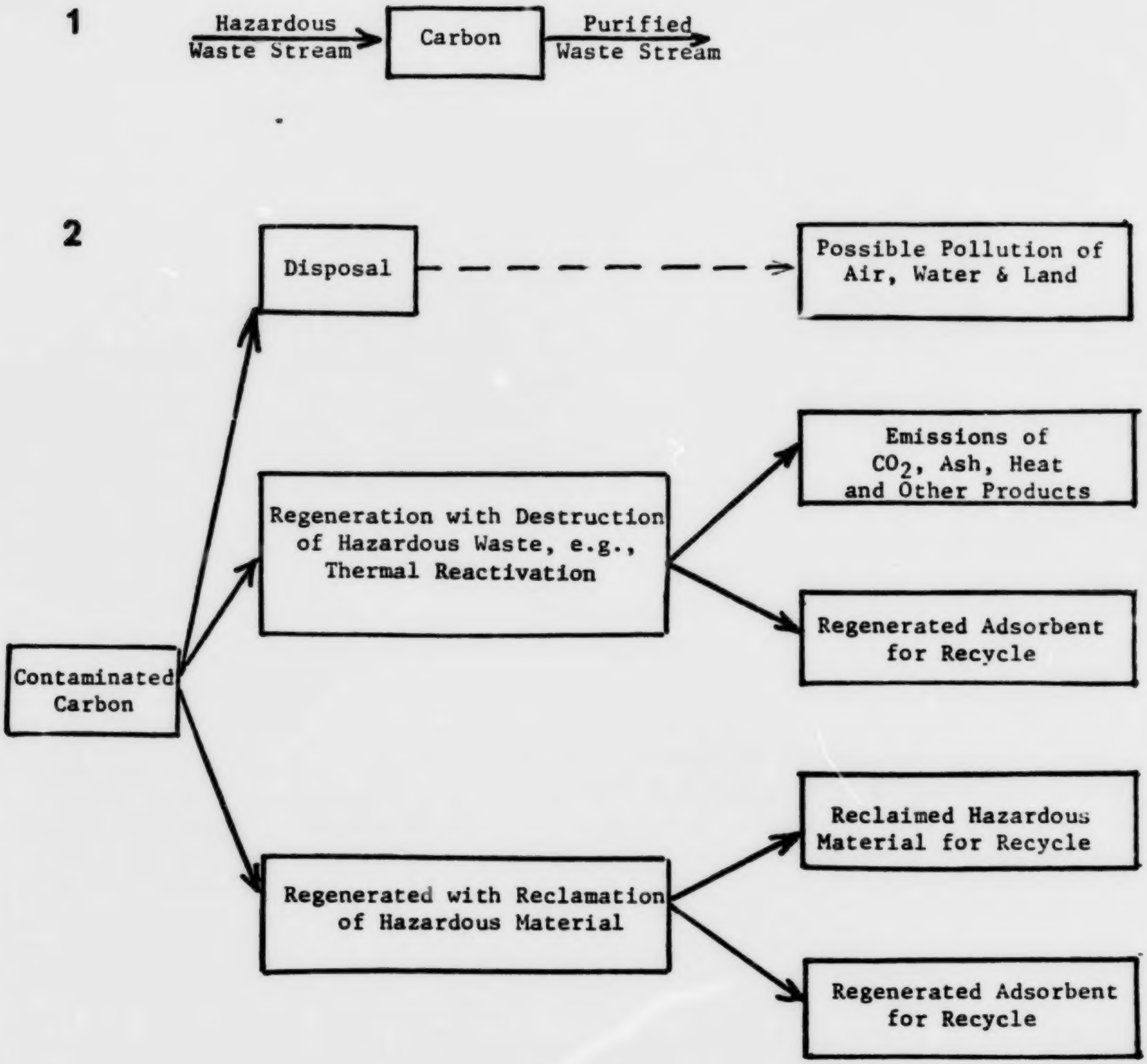
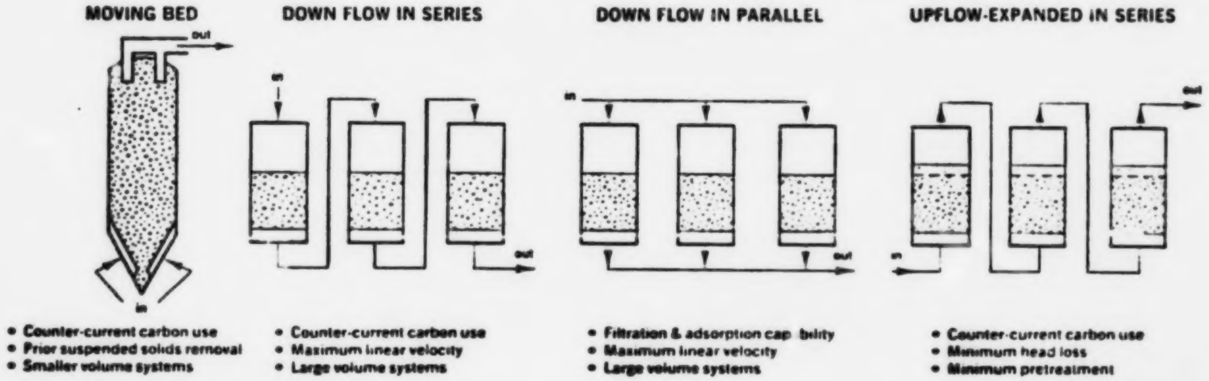

1
Hazardous Waste Stream
Carbon
Purified Waste Stream
2
Disposal
Possible Pollution of Air, Water & Land
Emissions of CO2, Ash, Heat and Other Products
Regeneration with Destruction of Hazardous Waste, e.g., Thermal Reactivation
Regenerated Adsorbent for Recycle
Contaminated Carbon
Reclaimed Hazardous Material for Recycle
Regenerated with Reclamation of Hazardous Material
Regenerated Adsorbent for Recycle

FIGURE 1 STEPS IN CARBON ADSORPTION

c. Contacting Systems

There are several ways that waste streams can be contacted with carbon, based on the choice of influent characteristics, effluent criteria, flow rate and economics. Four of the more common contacting methods, shown in Figure 2, are:

Method	**Comments**
Adsorbers in Parallel	• For high volume applications • Can handle higher than average suspended solids (~65-70 ppm) if downflow • Relatively low capital costs • Effluents from several columns blended, therefore less suitable where effluent limitations are low
Adsorbers in Series	• Large volume systems • Countercurrent carbon use • Effluent concentrations relatively low • Can handle higher than average suspended solids (~65-70 ppm) if downflow • Capital costs higher than for parallel systems
Moving Bed	• Countercurrent carbon use (most efficient use of carbon) • Suspended solids must be low (< 10 ppm) • Best for smaller volume systems • Capital and operating costs relatively high • Can use such beds in parallel or series
Upflow-expanded	• Countercurrent carbon use (if in series) • Can handle high suspended solids (they are allowed to pass through) • High flows in bed (~ 15 gpm/ft^2)



Source: Ref. 11.

FIGURE 2 ADSORBER CONFIGURATIONS

In the above systems, flow rates will generally be in the range of 2-10 gpm/ft^2 for downflow operation, 2-7 gpm/ft^2 for upflow operation (without expansion) and around 15 gpm/ft^2 for upflow – expanded with about 10% bed expansion. Downflow operation may be either by gravity or pressure; the former is clearly less expensive but only applicable if suspended solids in the influent are low.

Finally, there is an additional method of contacting which is significantly different from the types described above. Powdered or granular carbon can be added to a conventional biological wastewater treatment system (e.g., to the aeration basin) and yield significant improvements in pollutant removal (Ref. 12). This method is currently being used in at least three industrial waste treatment plants and one waste management facility. Contacting by this method may be followed by biological regeneration of the carbon. (See Section e below.)

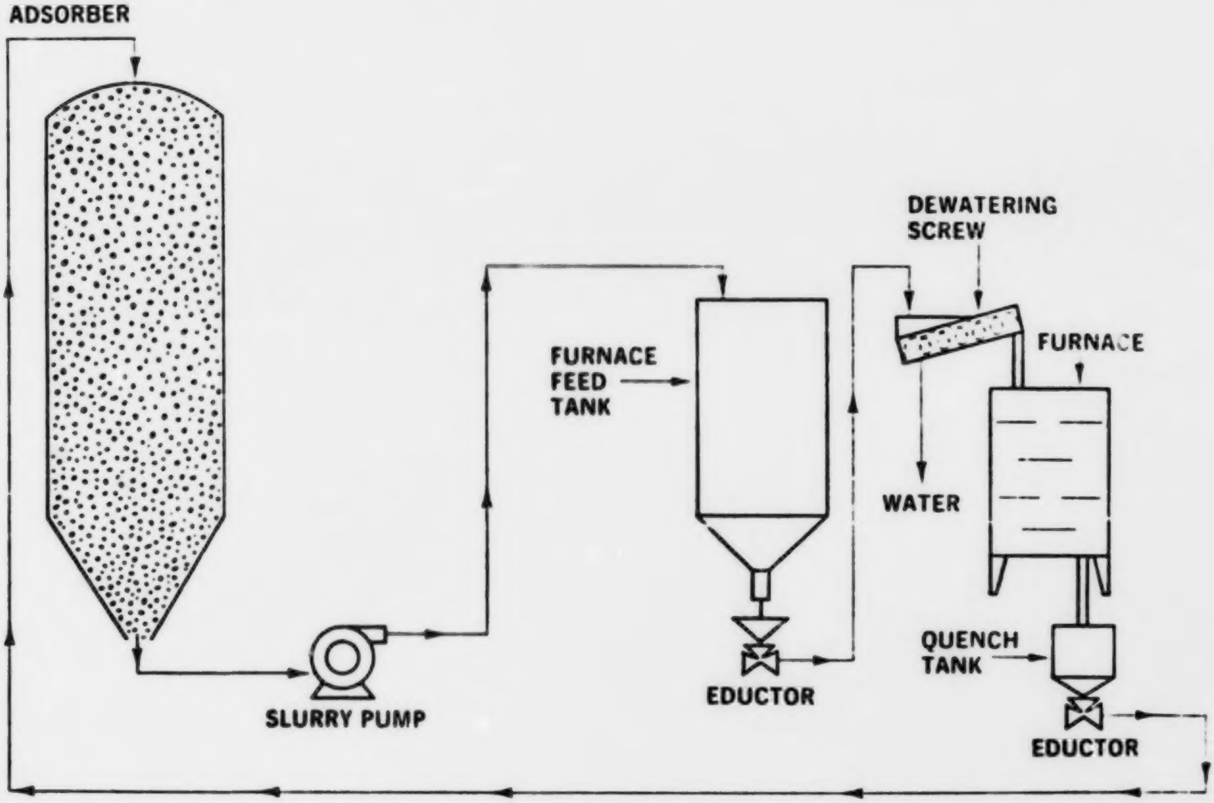
d. Backwashing Requirements

In some systems, contacting must be periodically stopped and the carbon column backwashed with water to remove suspended solids that have been filtered out of wastewater by the carbon bed. In the case of downflow contactors, which may be designed to act in part as a suspended solids filter, frequent backwashing with bed expansions of up to 50% may be required. The backwash water is usually recycled to the primary sedimentation for treatment.

e. Regeneration

If a large quantity of carbon is used (per unit time) then regeneration is carried out to recover and reactivate the carbon. The most common method is thermal reactivation (which destroys the adsorbed organic solutes), but non-destructive chemical regeneration may be possible in some cases. Some of the options are briefly described below. (More detailed information may be found in Ref. 13.)

(1) *Thermal Reactivation* – Reactivation is carried out in a multiple hearth furnace or a rotary kiln at temperatures from 870°C to 980°C as shown in Figure 3. Required carbon residence times in a furnace are of the order of 30 minutes. Steam is usually introduced to assist, the reactivation at the rate of 1 lb steam/lb of carbon. Fuel requirements are about 4000-5000 Btu/lb of carbon. With proper control, the carbon may be returned to its original activity; carbon losses will be in the range of 4%-9% and must be made up with fresh carbon. Afterburners (operating on the effluent vapors) to ensure complete destruction of organic compounds, followed by a scrubber to remove any particulates. An additional 2000-4000 Btu/lb of carbon may be required for operation of the afterburner.



Source: Ref. 11.

FIGURE 3 GRANULAR CARBON THERMAL REACTIVATION CYCLE

Sometimes thermal reactivation of granular carbons may not be possible; e.g., (1) when inorganic salts have deposited (or may deposit) on the carbon, though a preliminary acid wash may help avoid this problem; (2) when the carbon contains adsorbates that would cause air pollution problems upon regeneration (NO_x, radioactive materials, etc.); (3) when the adsorbates were explosive (e.g., TNT); or (4) when the loaded carbon was excessively corrosive.

(2) *Alkaline Regeneration for Acid Adsorbates* – In some industrial wastewaters, the major organic component is acidic, and adsorption, carried out under acidic conditions, may be followed by removal of the solute (i.e., regeneration) under basic conditions. This process has been successfully applied by Dow in Midland, Michigan, to recover phenol and acetic acid (Ref. 14-16). A similar process is in use in a large-scale plant by Sherwin Williams; adsorption of p-cresol is followed by desorption and recovery with a 10% NaOH stream (Ref. 17).

(3) *Acid Regeneration for Basic Adsorbates* – Certain basic adsorbates, adsorbed under basic conditions, may be recovered by washing with acid. This method has recently been found practical for the recovery of ethylene diamine at Dow Chemical Company (Ref. 18).

(4) *Solvent Regeneration* – If the adsorbate easily dissolves in an organic solvent, it may be washed off the carbon and recovered after separation from solvent, e.g., via distillation. There have been pilot-scale studies on organics adsorbed from coke plant flushing liquor followed by regeneration with hot benzene (Ref. 19) and demonstration tests have shown that acetic acid can be removed from carbon by regeneration with hot ethanol vapors (Ref. 20). In the latter case, the acetic acid is recovered as ethyl acetate; a demonstration unit (150-175 gpm) is currently being installed at the Flambeau Paper Company, Park Falls, Wisconsin.

(5) *Steam Regeneration* – If the adsorbate is volatile enough, recovery may be carried out by passing steam through the carbon bed.

(6) *Biological Regeneration* – Attempts have been made to utilize biological regeneration (Ref. 19, 21-25). The effectiveness of this method will clearly depend on the biodegradability of the adsorbed organics. Complete regeneration is not achieved, and thermal regeneration may be required periodically. The preferred mode of operation is to incorporate the carbon in a biological treatment system (for adsorption and assistance in biodegradation), recover the carbon with some activated sludge in the clarifier, and regenerate the carbon by aeration of the carbon/sludge mixture.

3. Output Streams

Air and water emissions from carbon adsorption units employing carbon regeneration are relatively innocuous. The treated water is generally suitable for discharge to surface waters but may, in some cases, require reaeration (to raise the level of dissolved oxygen), or other treatments to remove solutes not adsorbed by carbon. Other water streams associated with carbon systems (e.g., backwash, carbon wash and transport waters) are recycled or sent to a settling basin. Emissions will result from thermal reactivation, but when afterburners and scrubbers are used, the emissions are non-polluting. In some installations, particulates must be removed from this air stream (e.g., via a cyclone and baghouse) and this will result in a solid waste. Table 2 shows one example of air emissions from a carbon regeneration system.

TABLE 2

EMISSIONS FROM CARBON REGENERATION

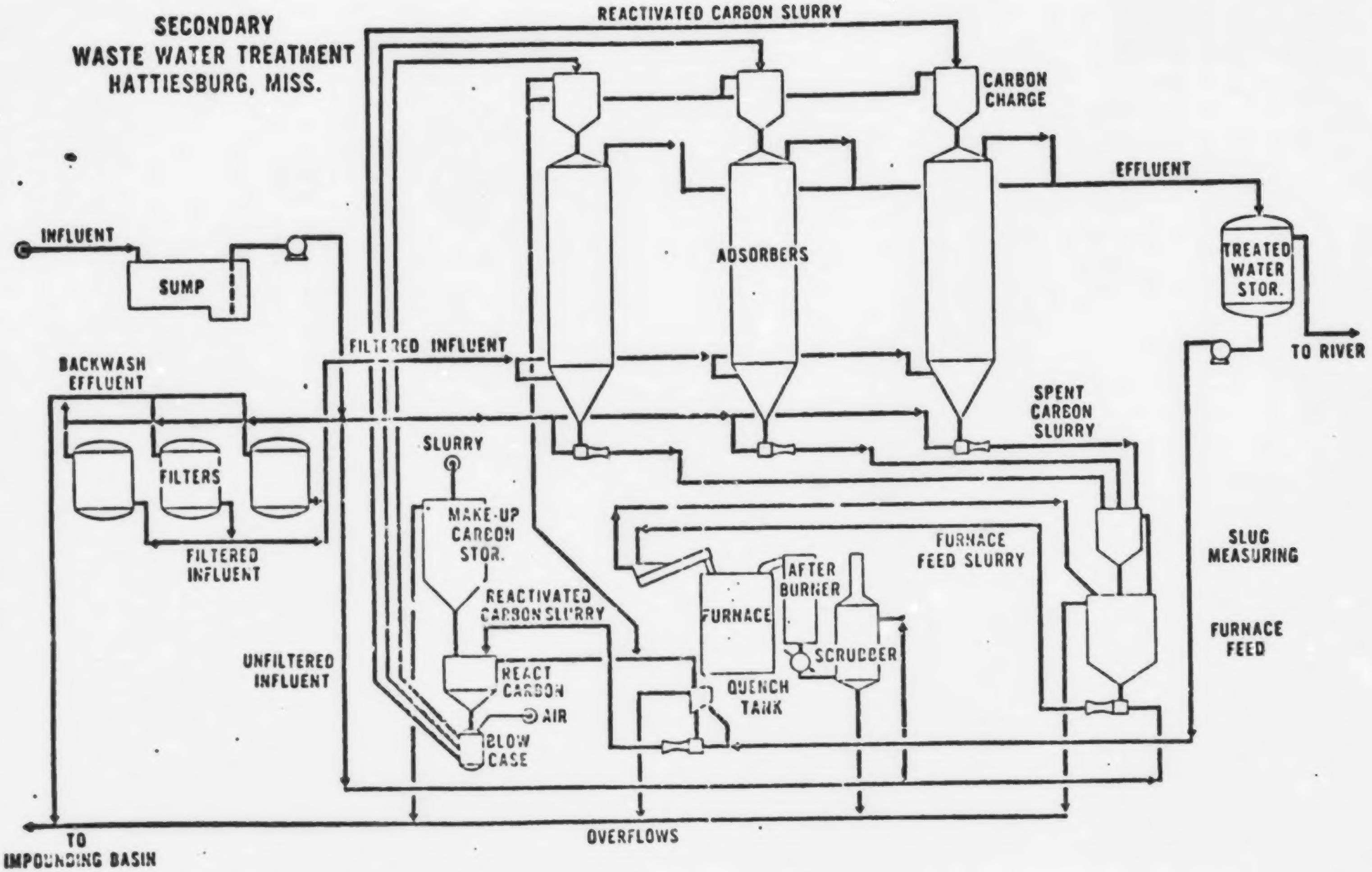
Pollutant		Los Angeles Co. Emission Limits	Baghouse Outlet	Afterburner Outlet
Particulates	Grains/SCF	0.2	0.298	0.0455
Nitrogen Oxide	PPM NO_2	225	–	166
Sulfur Dioxide	PPM SO_2	2000	–	217
Hydrocarbons	PPM C	none	3900	660
Carbon Monoxide	% vol. dry	–	0.56	0.20
Odor	Units/SCF	none	20,000	10

Source: Ref. 26

When carbon is not regenerated after use, then the loaded carbon must be discarded. This will arise when (1) carbon usage is small, i.e., regeneration is not economical, (2) the carbon was used to adsorb materials that are difficult to regenerate (e.g., carbon loaded with TNT cannot be thermally reactivated), or (3) the carbon contained adsorbates that would cause serious pollution problems upon regeneration (e.g., NO_x, radioactive materials). In the second example above, the current practice by the DOD at many installations is to burn the carbon containing the TNT in an open field.

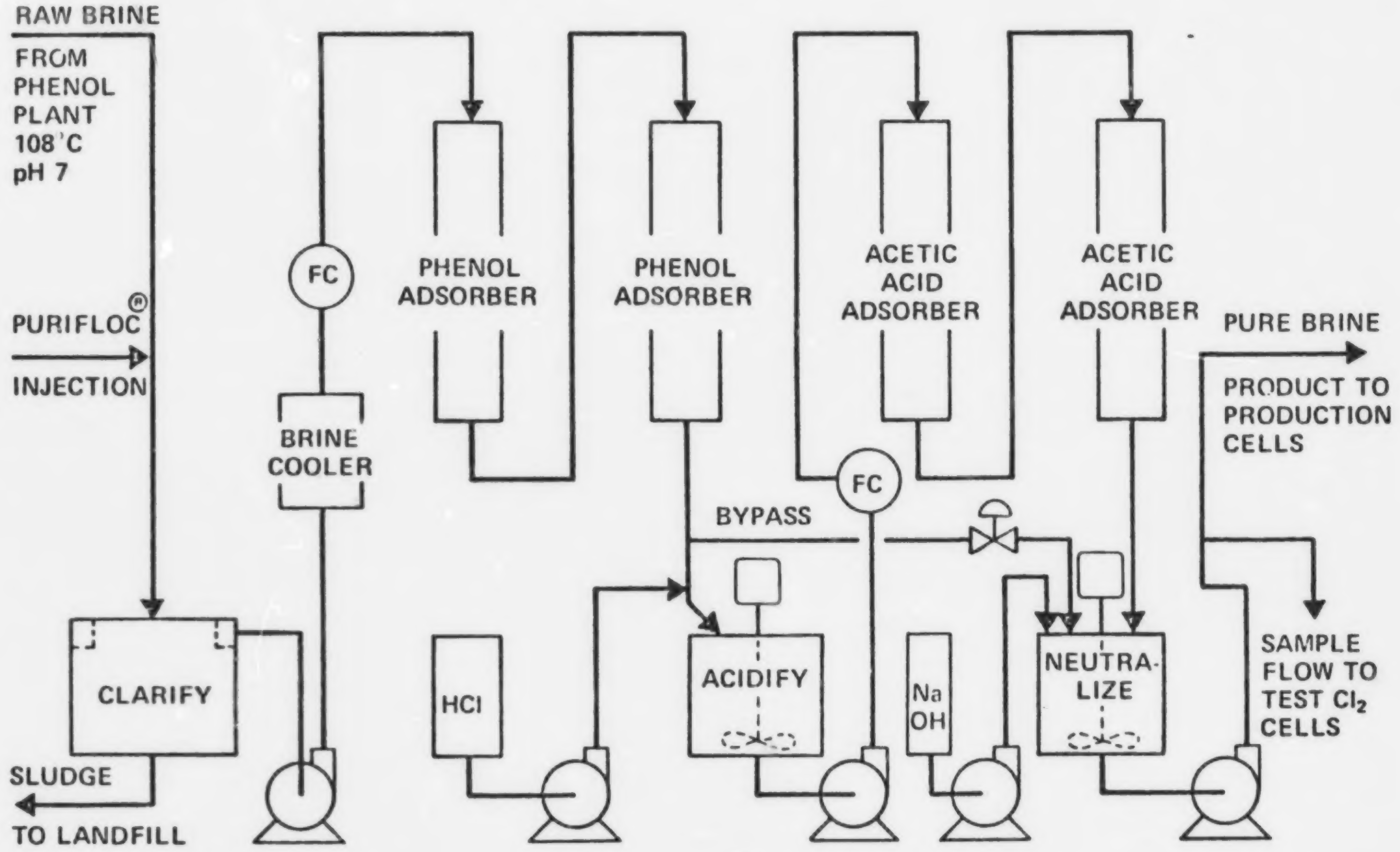
D. EQUIPMENT AND MATERIALS

The equipment needed for carbon adsorption systems can be quite complex and costly. Figure 4 shows a complete system incorporating thermal reactivation, and Figure 5 shows an adsorption system used in conjunction with caustic regeneration. In the latter case, regeneration takes place in the same tank as adsorption and, thus, the only equipment items (of the total system) missing from Figure 5 are the caustic feed tank, the sodium phenate receiving tank and associated pumps.



Source: Ref. 27.

FIGURE 4 SCHEMATIC DIAGRAM OF A CARBON ADSORPTION SYSTEM INCORPORATING THERMAL REGENERATION OF THE CARBON



Source: Ref. 16.

FIGURE 5 SCHEMATIC FLOWSHEET OF ADSORPTION PROCESS FOR PHENOL AND ACETIC ACID
(To Be Followed By Chemical Regeneration And Solute Recovery)

Tanks must be constructed of stainless steel or coated (rubber or epoxy) steel to prevent corrosion. If gravity contacting is possible, then cement may be used for adsorber construction. Additional details on specific design features are given in Ref. 28.

There are a wide variety of carbons currently available; the properties of four commercially available brands are given in Table 3. It is usually necessary to carry out laboratory tests with several different carbons before a final choice is made (e.g., adsorption capacity, resistance to abrasion, pressure drop in a column, ease of regeneration, etc.).

TABLE 3

PROPERTIES OF SEVERAL COMMERCIALLY AVAILABLE CARBONS*

PHYSICAL PROPERTIES	ICI AMERICA HYDRODARCO 3000	CALGON FILTRASORB 300 (8x30)	WESTVACO NUCHAR WV-L (8x30)	WITCO 517 (12x30)
Surface area, m^2/gm (BET)	600-650	950-1050	1000	1050
Apparent density, gm/cc	0.43	0.48	0.48	0.48
Density, backwashed and drained, lb/cu ft	22	26	26	30
Real density, gm/cc	2.0	2.1	2.1	2.1
Particle density, gm/cc	1.4–1.5	1.3–1.4	1.4	0.92
Effective size, mm	0.8–0.9	0.8–0.9	0.85–1.05	0.89
Uniformity coefficient	1.7	1.9 or less	1.8 or less	1.44
Pore volume, cc/gm	0.95	0.85	0.85	0.60
Mean particle diameter, mm	1.6	1.5–1.7	1.5–1.7	1.2
SPECIFICATIONS				
Sieve size (U.S. std. series)				
Larger than No. 8 (max. %)	8	8	8	–
Larger than No. 12 (max. %)	–	–	–	5
Smaller than No. 30 (max. %)	5	5	5	5
Smaller than No. 40 (max. %)	–	–	–	–
Iodine No.	650	900	950	1000
Abrasion No., minimum	**	70	70	85
Ash (%)	**	8	7.5	0.5
Moisture as packed (max. %)	**	2	2	1

* Other sizes of carbon are available on request from the manufacturers.

** No available data from the manufacturer.

– Not applicable to this size carbon.

Source: Ref. 28.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

The principal liquid-phase applications of activated carbon include (1) sugar decolorization, (2) municipal water purification (i.e., for water supply systems), (3) purification of fats, oils, foods, beverages and pharmaceuticals, (4) industrial/municipal wastewater treatment, and (5) other miscellaneous liquid-phase applications (Ref. 2).

It is estimated that there are roughly one hundred large-scale systems currently in use for industrial/municipal wastewater treatment; several are listed and briefly described in Tables 7 to 12 in Section VI-B of this report. Some additional comments on various waste treatment systems are given below.

1. Tertiary Treatment Plants (see Table 7)

Carbon adsorption, when applied to well-treated secondary effluent, is capable of reducing COD to less than 10 mg/l and the BOD to under 2 mg/l (Ref. 29). Removal efficiencies may be in the range of 30% to 90% and vary with flow variations and different bed loadings; for example, recent data from the South Lake Tahoe plant (Site 11, Table 7) show removal efficiencies vary from 30% to 60% (Ref. 30). Carbon loadings in tertiary treatment plants fall within the range of 0.25 to 0.87 lbs of COD removed/lb of carbon, and if the columns are operated downflow, over 90% suspended solids reduction may be achieved (Ref. 29).

It should be noted that all of the plants listed in Table 7 treat large flows (1-100 MGD), require contact times of around 30 minutes, and presumably use thermal reactivation.

2. Physical-Chemical Treatment (PCT) Plants (see Table 8)

Physical-chemical treatment acts on the effluent of a primary treatment system to remove BOD, COD, suspended solids, and (if present) some color. Effluent concentrations of BOD and COD are somewhat higher than for tertiary treatment systems. Carbon adsorption in conjunction with lime clarification (PCT) has been shown capable of achieving over 90% BOD and suspended solids reduction which is at least equivalent to secondary treatment (Ref. 29). Carbon loadings for PCT plants have been measured as high as 1.0 lb COD removed/lb carbon (Ref. 29) but will more typically be in the range of 0.4-0.6 lbs COD/lb carbon and 0.15-0.3 lbs TOC/lb carbon. It is clear that both tertiary and PCT plants have biological activity taking place in the carbon beds which increases the apparent carbon capacity. PCT plants currently being designed or constructed will have similar characteristics to tertiary treatment plants.

3. Treatment of Industrial Waste Streams (see Tables 9 to 12)

Quite frequently, segregated industrial waste streams are treated with activated carbon. The contaminants removed include BOD, TOC, phenol, color, cresol, polyethers, polynitrophenol, TNT, toluene, xylene, wood chemicals, p-nitrophenol, p-chlorobenzene, chlorophenols, resorcinol, xylol, insecticides, refinery wastes, cyanide, acetic acid, and other chemicals, mostly organic. The flows being treated are generally small in comparison with tertiary or PCT systems. Several systems treat less than 20,000 gpd, the lowest being 3,000 gpd. As indicated by Tables 10 and 11, thermal reactivation of the carbon is apparently used on some systems with flows as low as roughly 10,000 gpd, though this method of regeneration does not become common until flows are above about 60,000 gpd. The only systems with flows greater than 60,000 gpd that do not regenerate their carbon are (1) those where the carbon is added to the biological treatment system (2 plants) and (2) where TNT is present (1 plant). Some installations reactivate their carbon chemically and the adsorbate is recovered. Recoverable adsorbates are known to include phenol, acetic acid, p-nitrophenol, p-chlorobenzene, p-cresol, and ethylene diamine. Other adsorbates are recovered, but their identity has not been made known. Longer contact times are usually employed in such systems, e.g., 50-200 minutes, and in one case 540 minutes for a system that involves no pretreatment.

Carbon loadings approach 1 lb COD removal/lb carbon in installations where the adsorbates are easily adsorbed, biodegradable, and present in relatively high concentrations, e.g., a wood chemical plant that will use carbon to treat a stream containing about 700 ppm COD, and 200 ppm TOC; reductions are expected to be about 80% for both of these parameters (Ref. 27). In other cases where influent concentrations are lower, and where the adsorbates are not readily adsorbed, much lower loadings will result. For example, it was determined that brine wastewaters containing 150-750 ppm phenol and 1500-1800 ppm acetic acid could be reduced to about 1 ppm phenol and 100-200 ppm acetic acid with phenol loadings in the range of 0.09-0.16 lbs/lb and acetic acid loadings in the range of 0.04-0.06 lb/lb (Ref. 15). Another example related to the reduction of COD in refinery wastewaters from an average influent of 233 ppm to an average effluent of 48 ppm; the indicated loading in this case is 0.18 lb COD/lb carbon (Ref. 31). Other examples for loadings associated with removal of TOC, color and phenol are given for a wide variety of industrial effluents in Ref. 11.

Loadings for cyanide removal from electroplating wastes have been found to be on the order of 0.01 lb CN/lb carbon for influent concentrations around 100 ppm (Ref. 6). Loadings for removal of hexavalent chromium from electroplating wastes have been shown to be as high as 0.07 lb Cr/lb carbon at 100 ppm and 0.14 lb Cr/lb carbon at 1000 ppm (Ref. 7).

4. Carbon Treatment at Waste Management Facilities

At least two different waste management facilities use carbon as part of their waste treatment facilities. Chem-Trol Pollution Services, Inc. (Model City, New York) uses a granular carbon contacting system to remove BOD and COD associated with higher molecular weight organic chemicals. Flows are around 100,000 gpd; influent contains several thousand ppm of TOC. Sophisticated physical and chemical treatment of industrial wastes (obtained from about 500 different companies) precedes the carbon unit; an aeration basin and holding pond are used for final polishing after the carbon unit. The carbon unit is leased from Calgon Corporation, and used carbon is shipped to Calgon for reactivation.

At Hyon Waste Management Services, Inc. (Chicago, IL) carbon is added to the aqueous biological treatment system to assist in pollutant removal and to protect the system against shock from sudden increases in certain toxic pollutants.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Activated carbon has a wide range of potential applications for waste treatment, with the largest number for the removal (and eventual destruction) of mixed organic matter from aqueous wastes. A summary of potential areas of applicability is given in Table 4.

TABLE 4

POTENTIAL APPLICATIONS FOR WASTE TREATMENT WITH ACTIVATED CARBON

I. **Aqueous Wastes** – with adsorbate concentrations up to about 10,000 ppm; SS $\lesssim$ 50 ppm, 0 & G $\lesssim$ 10 ppm.

  A. **Organics** – Prefer chemicals with low solubility, low polarity, low degree of ionization. Problem chemicals include acetone, ethanol, glycol, soaps, etc., and others that are of low molecular weight and/or high solubility.

    (i) Regeneration –
      (1) *Thermal*, which destroys adsorbates, is economical if carbon usage is above roughly 1,000 lbs/day.
      (2) *Chemical*, may be used if one (or just a few) solute is present which can dissolve off the carbon. This allows material recovery.
      (3) *Biological*, if wastes are highly biodegradable. Virgin carbon activity not obtained after reactivation.

    (ii) Disposal – Disposal of the carbon may be required if use is less than ~1,000 lbs/day and/or a hazardous component mitigates against any form of regeneration.

  B. **Inorganics** – Cr and CN currently removed in industrial applications. Other possibilities, listed in Table 1, are somewhat limited. Strong electrolytes are not well adsorbed.

II. **Organic Wastes** – *Current Applications:* None known

Potential Applications: Removal of color, oil and grease, or other adsorbable impurities from solvents with resaleable potential.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements for carbon adsorption systems will depend not only on the size of the system, but also on the method and frequency of regeneration required. When thermal reactivation is used, significant amounts of electricity and fuel are used. At installations where reactivation is infrequent, total energy requirements may constitute less than 15% of total operating costs, and the electricity requirements associated with the adsorption process will account for most of these costs. For example, at the South Lake Tahoe unit (from 1969 to 1970), electricity requirements for the adsorption process accounted for about 11% of total operating costs, while gas and electricity requirements for the reactivation process amounted to only about 2% of total operating costs (Ref. 28). This system was reactivating about 1.3 tons of carbon per day, and the energy requirements associated with both adsorption and reactivation included the use of 4130 kWh/day of electricity and 113 therms of natural gas/day.

Other recent estimates for energy requirements where thermal reactivation is used indicate that energy costs are likely to be in the range of 10%-25% of total operating costs; this requirement would be higher if very concentrated streams were treated. Fuel requirements for the thermal reactivation of carbon (natural gas, propane, LPG, or fuel oil) total around 6,000-8,000 Btu per lb of carbon, including afterburner fuel.

When thermal reactivation of the carbon is not employed, then energy costs may not exceed 5% of total operating costs. For example, the carbon system at Dow, which includes chemical regeneration, has energy costs about 4% of total operating costs (Ref. 16). If the carbon is not regenerated, then energy requirements may be even less. In fact, this used carbon may have fuel value and could be used in heating systems capable of burning solid materials.

B. ENVIRONMENTAL IMPACTS

There are no serious environmental impacts from carbon systems using thermal reactivation since the only output streams are (1) a purified liquid (e.g., water), and (2) furnace gases, which have been through an afterburner and a scrubber, and in some cases, a dust filter.

Where the carbon is chemically regenerated, the major output streams consist of (1) the purified liquid, (2) a recovered material, and (3) used carbon, because carbon will lose some activity in successive chemical regenerations and will have to be replaced periodically. For example, the phenol recovery unit at Dow Chemical (Midland, Michigan) has required replacement of carbon beds about once every two years (Ref. 32). This waste carbon, which may be burned or buried, would constitute a minor environmental impact upon disposal.

In systems where the carbon is not regenerated at all, impacts could result from the disposal of the carbon, and possibly from contained toxic or hazardous materials.

C. ECONOMIC ANALYSIS

1. Introduction

There are several variables or alternatives in the design and operation of a carbon treatment unit, all of which can affect the economics. Included are:

- Type of carbon – granular or powdered
- Contact time
- Flow rate
- Configuration – series, parallel, or moving bed
- Number of stages
- Flow direction – packed or expanded, upflow or downflow
- Hydraulic force – pumped or gravity
- Carbon capacity
- Method of regeneration – thermal, chemical, none

Different carbon adsorption systems may result in unit costs (e.g., dollars/1000 gallons) that will vary by over two orders of magnitude. This report does not cover all system types or discuss the economic effect of all design variables; further information is given in Refs. 28 and 33. Some general considerations plus several examples of treatment costs for specific systems are given below.

2. General Considerations

a. Primary Variables*

Capital and operating costs for carbon systems employing thermal regeneration are a function primarily of two variables:

- *The carbon exhaustion rate*, usually expressed as pounds of carbon reactivated per volume of liquid treated; and,

- *Superficial liquid retention time*, i.e., the time that the liquid would take to fill the volume of the carbon bed. This is a direct function of the liquid flow rate and the carbon volume.

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*Much of this information is taken from Ref. 34.

The total capital cost is established by the volume of the carbon beds and the size of the reactivation furnace. The operating costs are determined by the carbon exhaustion rate since the largest variable is usually the cost of the make-up carbon. These two primary variables are related (for a specific system) and this relationship can be given as an "operating line" as shown in Figure 6a. The minimum exhaustion rate, the minimum retention time, and the curve itself may be obtained from laboratory data (e.g., from carbon isotherms and column studies). The general position of this curve will depend on the effluent quality desired, system configuration and other factors. For example, if a lower concentration effluent is required, the minimum exhaustion rate and retention time will increase and this will move the operating line further away from the origin. Also, a system using a countercurrent moving-bed will result in an operating line that is closer to the origin than a single fixed bed which makes less efficient use of the carbon.

Once the operating line is established, it is possible to select the combination of carbon exhaustion rate and liquid retention time which gives the optimum or lowest-cost design. For example, Figures 6b, 6c, and 6d illustrate the steps for determining the best combination of primary variables for the removal of ABS (alkyl benzene sulfonate) from water. In this system, 40 MGD of water are passed through large single-fixed-beds to reduce the ABS from 10 ppm to 1 ppm. Figure 6b shows two operating lines relating to 1 and 2 ppm ABS in the effluent. Figure 6c shows the capital costs as a function of superficial retention time, and Figure 6d shows both direct and total operating costs as a function of the same variable. The minimum total cost, for the 10% value of capital curve, is seen to be about $440,000/year; it would utilize a superficial retention time of about 15 minutes and an exhaustion rate of about 0.7 lb of carbon/1000 gallons. In this example, total operating costs are roughly 3¢/1000 gallons. Carbon treatment of hazardous wastes with much higher influent concentrations and much lower flows would be considerably more expensive.

b. Capital Cost Estimates

Once the optimum superficial retention time-exhaustion rate has been determined, the adsorption and reactivated portions of the system may be sized. Capital cost versus size curves are given in Ref. 28 (representative of relatively large units), and those data may be used – after accounting for inflation – to estimate capital costs.

c. Carbon Regeneration and Replacement Costs

Costs for thermally reactivating carbon rise rapidly as the volume regenerated falls below 1,000 lb/day and at some point regeneration will be more expensive than replacement. For high volume systems (e.g., more than 10,000 lbs of carbon regenerated per day), regeneration costs will be around 10-15¢/lb* and will not decrease substantially for larger systems. It should be noted that the capital costs for a thermal reactivation system in an

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*Arthur D. Little, Inc., estimates.

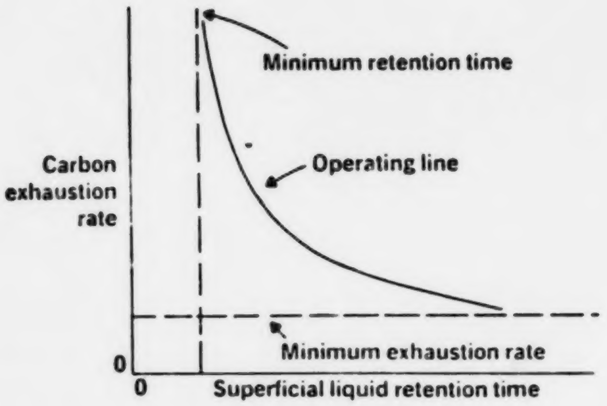

FIGURE 6a EXAMPLE OF OPERATING LINE PLOT

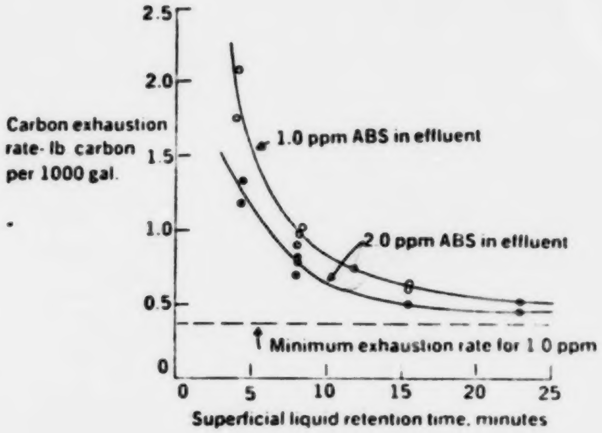

FIGURE 6b OPERATING LINE FOR ABS IN WATER

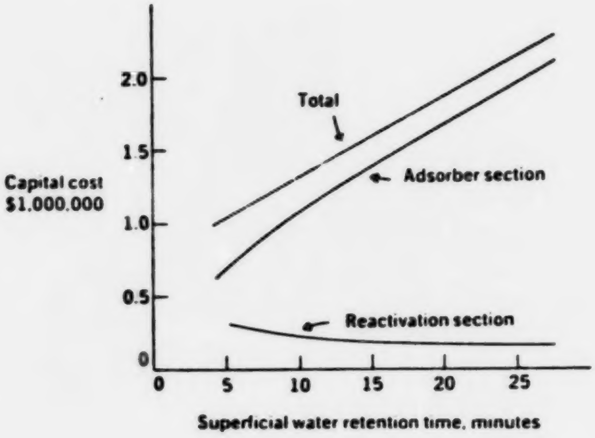

FIGURE 6c CAPITAL COST OF FACILITIES TO REMOVE ABS FROM WATER

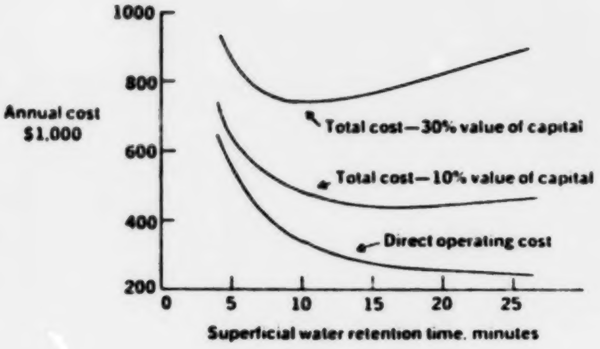

FIGURE 6d ANNUAL COSTS TO REMOVE ABS FROM WATER

Source: Ref. 34.

adsorption system treating relatively concentrated wastes (e.g., ~ 1,000 ppm adsorbate concentration) can amount to 45% to 50% of total capital costs. This percentage will increase as the adsorbate concentration increases. Current carbon costs range from around 30¢/lb for a pulverized carbon to 45¢ to 50¢/lb for a high-grade granular carbon.

d. Adsorption Services* – An Alternative to In-house Capital Investment

Since late 1972, Calgon Corporation has been offering a service to customers which involves the leasing of adsorption equipment and the regeneration of the carbon at a regional regeneration center. Calgon expects to have 30 to 40 customers and three regeneration centers by the end of 1976; two regeneration centers are currently in operation. Customer applications involve treatment of streams as small as 7 to 10 gpm and as high as several MGD. Almost any system configuration can be put together with the prefabricated units that are used for the adsorption system.

By the use of this service, a company can avoid all capital costs (except some site preparation costs) and instead pays a service fee. It is estimated (by ADL) that this annual service fee should be approximately the same as or slightly smaller than the total annualized operating costs (i.e., including equipment depreciation) of a company-owned facility operating with the same parameters. The service does benefit from economies associated with (1) the use of predesigned (and partially prefabricated) units, (2) quantity purchases of carbon, and (3) volume regeneration. These are offset by the costs of trucking the carbon between the customer and the center, and by the fee that Calgon would retain.

3. Some Examples of Carbon Treatment Costs

a. Phenol Removal (without recovery)

This hypothetical example is based on the following parameters:

Influent Stream:

Flow: 100,000 gpd
Phenol content: 1,000 ppm
Limitations: suspended solids <10 ppm; oil and grease <10 ppm

Treatment Objective: <1.0 ppm phenol

Adsorbent: Activated Carbon
Cost: 50¢/lb

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*Service mark of Calgon Corporation, Pittsburgh, Pennsylvania.

Phenol Loading: 0.12 lbs phenol/lb carbon

Carbon Loading: 70 lbs carbon/1000 gallons of water treated

Adsorption System (similar to that shown in Figure 4)

- Total of 3 adsorption tanks, each 8 feet in diameter x 20 feet high, and made of 304 stainless steel.
- Each, when in use, loaded with 19 feet of carbon, or about 28,000 lbs.
- Adsorption flow is downflow in series through two columns; the second of these acting as a polishing column. Third column out of service for carbon regeneration. Pipes for any combination.

TYPICAL CYCLE SCHEDULE

Day	Column A	Column B	Column C
0-4	1st Adsorber	2nd Adsorber	(Regenerate)
5-8	(Regenerate)	1st Adsorber	2nd Adsorber
9-12	2nd Adsorber	(Regenerate)	1st Adsorber

Operation Periods: 24 hours/day; 330 days/yr

Furnace:

Type: Multiple hearth, gas fired
Capacity: Designed to handle 14,000 lbs of carbon/day which includes an over-design factor of two
Actual regeneration: 7,000 lbs of carbon/day
Carbon losses/pass: 7.5% (525 lbs/day)
Steam requirements: 1 lb steam/lb of carbon
Total fuel requirements: ~ 7580 Btu/lb of carbon

Other Equipment Items Required (see Figure 4):

Sump, slurry, pumps, carbon charge tanks, slug measuring tank, furnace feed tank, afterburner, scrubber, quench tank, make-up carbon storage tank, reactivated carbon tank, blow case tank w/air supply, dewatering screw, treated water storage tank.

The estimated capital and operating costs for this system are given in Table 5. Total investment is estimated to be $1,200,000 – about half of which is related to the thermal reactivation system – and total operating costs are just over $17/1,000 gallons ($2/lb of phenol).

TABLE 5

ESTIMATED COST FOR ACTIVATED CARBON REMOVAL OF PHENOL

Basis: 100,000 GPD, 1,000 ppm Phenol; 330 days/yr Operation

Estimated Investment: $1,200,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Labor	11,500 MH	$12/hr	$138,000
Maintenance (5% of Inv)			60,000
Electricity	700 x 10^3 kWh	$0.02/kWh	14,000
Steam	2.35 x 10^6 lb	$4.00/$10^3$ lb	9,500
Fuel	17.5 x 10^9 Btu	$2.25/$10^6$ Btu	39,500
Carbon Make-up	174 x 10^3 lb	$0.50/lb	87,000
TOTAL VARIABLE COSTS			$348,000
Fixed Costs			
Taxes and Insurance (2% of Inv)			24,000
Capital Recovery (10%-10 Yrs)			195,000
TOTAL FIXED COSTS			$219,000
TOTAL COSTS			$567,000
Unit Cost – ($/1000 gallons)			17.18
Unit Cost – ($/lb of Phenol)			2.06

Source: Arthur D. Little, Inc., estimates

b. Phenol and Acetic Acid Removal With Recovery of Phenol

The costs of removing and chemically recovering phenol from a 100 gpm (144,000 gpd) brine stream containing 150-750 ppm phenol and 1400-2000 ppm sodium acetate have been given following the installation and demonstration of such a unit at the Dow Chemical Company, Midland, Michigan (Ref. 16). This report, from 1973, put capital requirements at $692,000 and total operating costs, before credits, at just over $5/1000 gallons. A breakdown of these operating costs is given in Table 6.

TABLE 6

PROJECTED COSTS FOR PURIFICATION OF 100 GAL/MIN OF PHENOL PLANT WASTE BRINE

	$/1000 Gal
Depreciation @ $69,200/yr (10 yr straight line)	$1.45
Maintenance @ $25,000/yr	0.52
Utilities @ $8,600/yr	0.18
Chemicals	2.17
Labor (incremental with automation)	0
Carbon Make-up	0.70
Total Projected Costs	**$5.02**
Credits	
Recovery of phenate regenerant	$1.05
Salt recycle	1.00
Reduction of brine disposal cost	1.65
Total Credits	**$3.70**
Net Operating Cost	**$1.32**

Source: Reference 16

The major cost items are seen to be depreciation, the caustic soda required for regeneration, and carbon.

At present, this system is operating only on a phenol-containing brine, i.e., there is no acetic acid to remove. Carbon replacement has been required about once every two years – which is twice as long as the assumed yearly replacement that went into the carbon make-up costs in Table 6. The system requires the attention of one man, half-time while in operation (Ref. 32).

c. Herbicide Removal (Ref. 35)

One industrial plant that manufactures herbicides (2,4-D Acid, MCPA Acid, and 2,4-DB Acid) installed a carbon treatment unit (in 1969) to treat a 150,000 gpd waste stream containing 10 ppm phenol and cresol, 100 ppm chlorophenols and chlorocresols, 100 ppm chlorophenoxyacetic acids, 1000 ppm alcohols (primarily octyl), plus high levels of dissolved inorganic salts (62,000 ppm total solids) and relatively high levels of BOD (2000 ppm) and COD (3600 ppm). This unit discharges to a municipal treatment plant and, thus, must reduce phenolics to less than 1 ppm.

The system employs two upflow carbon beds, in series, and contact time is 140 min/bed. Each adsorber contains 18,000 lbs of carbon. The carbon is thermally reactivated. The estimated capital investment for this system was $300,000, including $40,000 for an effluent neutralization system and $30,000 for a water collection system. Direct operating costs were given (in 1972) as $0.36/1000 gallons.

d. Complex Chemical Plant Wastewaters (Ref. 27)

A naval stores plant, which uses wood to produce a wide variety of wood chemicals, installed a carbon treatment unit in 1973 to treat their 2.6 MGD wastewater stream. After primary treatment, the influent to the carbon unit contains about 700 ppm COD, 200 ppm TOC, 250 ppm BOD, 50 ppm suspended solids (SS) and 650 ppm dissolved solids (DS). The effluent from the carbon system contains about 125 ppm COD, 30 ppm TOC, 50 ppm BOD, 5 ppm SS, and 400 ppm DS; this is about an 80% reduction of dissolved organics.

The carbon system for this application is shown in Figure 4. Flow is upflow (~ 7 gpm/ft^2) through a packed bed with countercurrent carbon flow and adsorbers operating in parallel. Carbon contact time is about 50 minutes and carbon loadings are in the range of 0.6 to 0.9 lb of COD/lb of carbon.

Capital costs for this system were estimated to be $1,781,000, and operating costs were initially estimated to be about $182,000/yr. Actual operating costs have turned out to be somewhat larger and are given as 31.4¢/1000 gallons, not including capital depreciation. Total operating costs, including depreciation, are thus around 60¢/1000 gallons.

e. Refinery Effluents (Ref. 31)

In recent EPA-sponsored tests, carbon adsorption was demonstrated to be feasible for COD reduction in refinery wastewaters. Average influent concentration was 233 ppm COD, and average effluent concentration was 48 ppm COD. Carbon loading was about 9 lbs of carbon/1000 gallons of water, or 0.25 lbs of COD/lb of carbon. In a two year test period, 172,040,000 gallons were treated, and direct operating costs averaged 49¢/1000 gallons (or 24¢/lb of COD removed). During the second year of operation, the efficiency increased and direct operating costs reduced to 40¢/1000 gallons (or 18¢/lb of COD removed).

f. Chromium Recovery From Electroplating Wastes (Ref. 7)

Operating costs for a carbon process employing caustic regeneration were estimated (in 1971) to be about $5.00 per 8-hour day on the basis of a 15 gpm waste stream containing 100 ppm of hexavalent chromium. This was compared to an operating cost of about $7.00 for the conventional treatment method employing sodium bisulfite.

Chromium loading capacities at this concentration were found to be in the range of 0.02 to 0.05 lb of chromium/lb of carbon, with the higher values being obtained at lower pH values (pH 2-3). Such a system can operate with removal efficiencies greater than 99% for hexavalent chromium.

g. Cyanide Removal From Electroplating Wastes (Ref. 6)

Estimates of capital requirements and net operating costs were prepared (in 1971) for both a manually controlled and for a semi-continuous carbon adsorption process for removing cyanides from plating rinse waters. The estimates were based on a wastewaster flow of 10 gpm containing 300 ppm of cyanide:

	Manually Operated System	**Semi-Continuous System**
Capital Costs ($)	12,000	16,000
Cost of Chemicals ($/lb CN)	0.30	0.30
Net Operating Costs ($/lb CN)	0.21-0.87	0-0.82

The range in net operating costs depends upon the amount of the credit that can be taken for recovery of copper as copper sulfate. The lower estimate of net operating costs accounts for the recovery of copper from the treatment of copper plating rinse waters.

Removal efficiencies in this system are over 99% for total cyanide.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

The *major benefits* of carbon treatment include:

- High organics removal
- Applicability to a wide variety of organics
- Capability for inorganics removal (e.g., CN, Cr, and others)
- Possible material recovery of organics and inorganics in a few cases (e.g., phenols, acetic acid, ethylene diamine, Cr, and others)
- High flexibility (e.g., rapid start-up and shut-down)
- Low sensitivity to feed variations (flow rate or concentration)
- Insensitivity to toxic materials
- Minimum land area
- Destruction of wastes when using thermal regeneration.

The *major limitations* of carbon treatment include:

- Relatively high capital and operating costs, especially when thermal reactivation is used
- Limited, generally, to wastes with less than about 1% organic content, or less than about 5% if adsorbates are to be recovered
- Cost savings associated with thermal reactivation may only be realized if carbon usage is above about 1000 lbs/day or if a centralized reactivation facility is available
- If carbon cannot be regenerated thermally or chemically, then it must be disposed of
- Low tolerance of suspended solids – should be less than about 50 ppm to reduce need for frequent backwashing
- Inability to remove low molecular weight and/or highly soluble organic chemicals (e.g., methanol, ethanol, glycol, soaps, etc.)
- Problems with thermal reactivation systems.

There are certain process modifications which may improve the applicability of the process. One is the upflow, expanded-bed flow configuration – now being used at only one full-scale facility – which has the capability of handling much higher levels of suspended solids. Another is the use of powdered carbon which is cheaper than granular carbon, and may have higher adsorption capacity, but, until recently, was not economical to regenerate because of high losses (around 15%). New processes currently being developed for the regeneration of powdered carbon may be capable of keeping losses below 10%.

Carbon adsorption must be considered a viable and economical process for organic waste streams containing up to 1-5% of refractory or toxic organics; its applicability for inorganics removal, though demonstrated in a few cases, is probably much more limited.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD (Partial Listing)

1. Experts

Mr. Joseph Rizzo, Calgon Corporation, Pittsburgh, Pennsylvania (company manufactures activated carbon, assists in system design, and offers an adsorption service).

Other carbon suppliers with markets in the water purification area will be able to offer expertise; included are (partial listing): Husky Industries, Inc.; ICI America, Inc.; Westvaco Corporation; Witco Chemical Corporation.

Leon H. Myers, U.S. EPA, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma (several studies of industrial waste treatment have been done by or for this laboratory).

Professor Walter J. Weber, Jr., University of Michigan, Ann Arbor, Michigan (Professor Weber is the author of research and survey papers on carbon treatment, and is a well-known consultant in this field).

2. Full-Scale Installations Using Carbon Adsorption

The following tables (Tables 7-12) list a large number of activated carbon treatment plants, not all of which are currently operating. Some, for example, are still in the design or construction stage. This listing is far from being a comprehensive list of all carbon adsorption systems for wastewater treatment, but will serve to identify the types of wastes that are being treated, the range of flow rates being treated, and other parameters associated with such systems. There are several duplications in these tables.

TABLE 7

TERTIARY TREATMENT PLANTS

SITE	STATUS 1973	DESIGN ENGINEER	AVERAGE PLANT CAPACITY (MGD)	CONTACTOR TYPE	NO OF CONTACTORS IN SERIES	CONTACT TIME(1) (MIN.)	HYDRAULIC LOADING (GPM/SQ.FT.)	TOTAL CARBON DEPTH (FT.)	CARBON SIZE	EFFLUENT REQUIREMENTS(2) (OXYGEN DEMAND)
1. Arlington, Virginia	Design	Alexander Potter Assoc.	30	Downflow Gravity	1	38	2.9	15	8 x 30	BOD < 3 mg/l
2. Colorado Springs, Colo.	Operating Dec. '70 to Present	Arthur B. Chafet & Assoc.	3	Downflow	2	30	5	20	8 x 30	BOD < 2 mg/l
3. Dallas, Texas	Design	URS Forest & Cotton	100	Upflow Packed	1	10	8	10	8 x 30	BOD <10 mg/l BOD < 5 mg/l (by 1980)
4. Fairfax County, Va.	Design	Alexander Potter Assoc.	36	Downflow Gravity	1	36	3	15	8 x 30	BOD < 3 mg/l
5. Los Angeles, Calif.	Design	City of Los Angeles	5(3)	Downflow Gravity	2	50	4	26	8 x 30	COD <12 mg/l
6. Montgomery County, Md	Design	CH2M/Hill	60	Upflow Packed	1	30	6.5	26	8 x 30	BOD < 1 mg/l COD <10 mg/l
7. Occoquan, Va.	Design	CH2M/Hill	18	Upflow Packed	1	30	5.8	24	8 x 30	BOD < 1 mg/l COD <10 mg/l
8. Orange County, Calif.	Construction	Orange County Water District	15	Upflow Packed	1	30	5.8	24	8 x 30	COD <30 mg/l
9. Piscataway, Md.	Operating Mar. '73 to Present	Roy F. Weston	5	Downflow Pressure	2	37	6.5	32	8 x 30	BOD < 5 mg/l
10. St. Charles, Missouri	Construction	Moran and Cooke	5.5	Downflow Gravity	1	30	3.7	15	8 x 30	
11. South Lake Tahoe, Calif.	Operating Mar. '68 to Present	CH2M/Hill	7.5	Upflow Packed	1	17	6.2	14	8 x 30	BOD < 5 mg/l COD < 30 mg/l
12. Windhoek, South Africa	Operating Oct. '68 to Present	National Institute for Water Research Pretoria, So. Africa	1.3	Downflow Pressure	2	30	3.8	15	12 x 40	COD < 10 mg/l

(1) Empty bed (superficial) contact time for average plant flow

(2) BOD Biochemical oxygen demand
COD Chemical oxygen demand

(3) 50 mgd ultimate capacity

Source: Ref. 28

TABLE 8

PHYSICAL CHEMICAL TREATMENT PLANTS

SITE	STATUS 1973	DESIGN ENGINEER	AVERAGE PLANT CAPACITY (MGD)	CONTACTOR TYPE	NO. OF CONTACTORS IN SERIES	CONTACT TIME[1] (MIN.)	HYDRAULIC LOADING (GPM/SQ.FT.)	TOTAL CARBON DEPTH (FT.)	CARBON SIZE	EFFLUENT REQUIREMENTS[2] (OXYGEN DEMAND)
1. Cortland, N.Y.	Design	Stearns & Wheler	10	Downflow Pressure	1 or 2	30	4.3	17	8 x 30	TOD < 35 mg/l
2. Cleveland Westerly, Ohio	Design	Engineering-Science	50	Downflow Pressure	1	35	3.7	17	8 x 30	BOD < 15 mg/l
3. Fitchburg, Mass.	Construction	Camp Dresser & McKee	15	Downflow Pressure	1	35	3.3	15.5	8 x 30	BOD < 10 mg/l
4. Garland, Texas	Design	URS Forest & Cotton	30[3]	Upflow Downflow	2	30	2.5	10	8 x 30	BOD < 10 mg/l
5. LeRoy, New York	Design	Lozier Engineers	1	Downflow Pressure	2	27	7.3	26.8	12 x 40	BOD < 10 mg/l
6. Niagara Falls, N.Y.	Design	Camp Dresser & McKee	48	Downflow Gravity	1	20	3.3	9	8 x 30	COD < 112 mg/l
7. Owosso, Michigan	Design	Ayres, Lewis, Norris & May	6	Upflow Packed	2	36	6.2	30	12 x 40	BOD < 7 mg/l
8. Rosemount, Minn.	Construction	Banister, Short, Elliot, Hendrickson, and Associates	0.6	Upflow Downflow Pressure	3 (max.)	66 (max.)	4.2	36 (max.)	12 x 40	BOD < 10 mg/l
9. Rocky River, Ohio	Construction	Willard Schade & Assoc.	10	Downflow Pressure	1	26	4.3	15	8 x 30	BOD < 15 mg/l
10. Vallejo, Calif.	Design	Kaiser Engineers	13	Upflow Expanded	1	26	4.6	16	12 x 40	BOD < 45 mg/l (90% of time)

(1) Empty bed (superficial) contact time for average plant flow

(2) BOD: Biochemical oxygen demand
COD: Chemical oxygen demand
TOD: Total oxygen demand

(3) 90 mgd ultimate capacity

Source: Ref. 28

TABLE 9

SUMMARY OF INDUSTRIAL SOURCES USING GRANULAR ACTIVATED CARBON SYSTEMS

Industry	Location	Principal Product	Contaminant(s) Removed
1. Velvet Textiles	Blackstone, VA	Velvet	Dyes, Detergents, Organics
2. BASF Wyandotte Chemical Corp.	Washington, NJ	Polyethers	Polyethers (MW 1000-3000)
3. ARCO-Watson Refinery	Wilmington, CA	Refinery Products	COD
4. Stephen Leedom	Southhampton, PA	Carpet Mill	Dyes
5. Reichhold Chemicals, Inc.	Tuscaloosa, AL	Phenol, Formalydehyde, Pentaerythritol, Orthophenylphenol, synthetic resins, and plastics	COD, Phenols
6. Schnectady Chemicals, Inc.	Rotterdam, NY	Phenolic Resins	Phenols
7. Chipman Div. of Rhodia, Inc.	Portland, OR	Herbicides-2,4-D acid, MCPA acid, 2, 4-DB acid and esters of these products	COD, Phenols
8. Sherwin-Williams Co.	Chicago, IL	p-Cresol	p-Cresol
9. Mobay Chemical Co.	Houston, TX	----	Color
10. Burlington Army Ammunition Plant	Burlington, IA	Explosives	TNT
11. Stepan Chemical Co.	Bordentown, NJ	Intermediate Detergents	Color and organics
12. Georgia Pacific	Conway, NC	Phenolic Resins	Phenols
13. Stauffer Chemical	Skaneateles Falls, NY	Strong Alkaline Detergents	COD
14. General Electric Co.	Selkirk, NY	Plastics	Phenols and COD
15. C.H. Masland & Sons	Wakefield, RI	Carpet Yarn	Color and COD
16. St. Regist Paper Co.	Pensacola, FL	Kraft products	Color
17. Monsanto Industrial Chemicals	Anniston, AL	Intermediate Organic Chemicals (polynitrophenol)	Polynitrophenol
18. Hercules, Inc.	Hatiesburg, MS	Acid Resins, turpines & solvents	Organics
19. Dow Chemical	Midland, MI	Phenol	Phenols and Acetic Acid
20. Hardwicke Chemical Co.	Elgin, SC	Intermediate and Specialty Organic chemicals	COD, Color
21. Crompton and Knowles Corp.	Gibraltar, PA	Dyes	Dye, COD

Source: Ref. 36

TABLE 10

FULL-SCALE ACTIVATED CARBON SYSTEMS TREATING ORGANIC CHEMICAL WASTES

Company	Granular systems	Wastewater flow, gpd	Contaminants removed	Reactivation scheme	Comments
Allied Chemical Birmingham, Ala.	Hydrodarco 4000	3,000	Phenols	None	.....
Dow Chemical Midland, Mich.	Witco 718	145,000	Phenols	4% NaOH	Removes phenols from 18% brine solution for use in chlor/alkali plant. Reactivation solution recycled to phenol plant
East Coast Manufacturer N.J.	Filtrasorb 400	58,000	Polyethers	Thermal	Discharges to municipal system
General Electric Pittsfield, Me.	Filtrasorb 300	Batch treatment (varies with use)	Color	Thermal	Used for treating a variety of waste stream in-plant. On-stream December 1971
General Electric Selkirk, N.Y.	Filtrasorb 300	300,000	Phenolics Toluene Color	Thermal	.....
Hardwicke Chemicals Elgin, S.C.	Filtrasorb	20,000	Mixed organics	Thermal	Subscribes to Calgon Adsorption Service
Hercules Chemicals Hattiesburg, Miss.	Filtrasorb 400	3,200,000	COD Mixed organics Wood sugars	Thermal	Just completing start-up
Monsanto Anniston, Ala.	Filtrasorb 300	65,000	*p*-nitrophenol *p*-chlorobenzene	Chemical	Reactivation chemical with recovered product returned to process
Rhodia, Inc. Portland, Ore.	Filtrasorb 400	150,000	Chlorophenols	Thermal	.....
Schenectady Chemicals Schenectady, N.Y.	Filtrasorb 300	22,000	Phenols Resorcinol Xylol	Thermal	On stream March 1973
Stephan Chemical Co. Fieldsboro, N.J.	Filtrasorb 300	15,000	Mixed organics associated with liquid detergent intermediates	Thermal	On-stream June 1972
Stauffer Chemicals Skaneateles Falls, N.Y.	Filtrasorb 300	8,000	COD from washout of batch equipment used to make mixed detergents and wash compounds	Expended carbon saved and shipped to central processing facility where a tank car load is accumulated	Treats segregated waste side-stream. Effluent then joins main waste stream

Source: Ref. 17

TABLE 10 (continued)

FULL-SCALE ACTIVATED CARBON SYSTEMS TREATING ORGANIC CHEMICAL WASTES

Company	Granular systems	Wastewater flow, gpd	Contaminants removed	Reactivation scheme	Comments
Reichhold Chemicals Tuscaloosa, Ala.	Filtrasorb 300	500,000	Phenols, BOD, COD	Thermal	Treats concentrated waste resulting from extensive in-plant water use reduction. On-stream late 1972
Sherwin-Williams Chicago, Ill.	Nuchar WV-G, 12 × 40	65,000	p-cresol	10% NaOH	.....
Vicksburg Chemical Vicksburg, Miss.	Hydrodarco 4000	10,000	Phenols	NaOH	.....
Ashland Chemicals Great Meadows, N.J.	Hydrodarco*	140,000	Color, COD	None	Biological treatment with 85 ppm of carbon added to influent
Dow Chemical Midland, Mich.	Nuchar*	14,000,000	Mixed organics	None	Biological treatment with carbon added to influent
Koppers Chemical Follunsbee, W.Va.	Nuchar*	20,000	Phenolics	None	Used when biological treatment efficiency drops

*Powdered system.
Source: P.S. Minor

TABLE 11

INDUSTRIAL WASTEWATER TREATMENT GRANULAR ACTIVATED CARBON INSTALLATIONS

Industry Location	Installation Date	Design Flow Rate (000 gals/day)	Organic Contaminants	Pretreatment	Adsorption System		
					Contact Time (minutes)	Adsorber Type	Carbon Reactivation
1 Carpet Mill British Columbia	6/73	50	Dyes	Screens		Moving Bed	None
2 Textile Mill Virginia	7/70	60	Dyes	Filtration	57	Moving Bed	None
3 Oil Refinery California	3/71	4200	COD	Equalization Oil Flotation	60	Gravity Beds In Parallel	Multiple Hearth Furnace
4 Oil Refinery Pennsylvania	3/73	2200	BOD	Equalization Oil Flotation Filtration		Moving Bed	Multiple Hearth Furnace
5 Detergent New Jersey	6/72	15	Xylene Alcohols TOC	None	540	Downflow Beds In Series	Multiple Hearth Furnace
6 Chemicals Alabama	11/72	500	Phenolics Resin Intermediates	Chemical Clarification	17.3	Moving Beds	Multiple Hearth Furnace
7 Resins New York	3/73	22	Xylene Phenolics Resorcinol	Chemical Clarification	30	Downflow Beds In Series	Rotary Kiln
8 Herbicide Oregon	11/69	150	Chlorophenols Cresol	None	105	Upflow Beds in Series	Multiple Hearth Furnace
9 Chemicals New York	3/69	15	Phenol COD	Equalization	200	Downflow Beds In Series	None
10 Chemicals Texas	11/71	1500	Nitrated Aromatics	Activated Sludge Filtration	40	Moving Beds	Rotary Kiln
11 Chemicals New Jersey		100	Polyols	Equalization Clarification		Moving Bed	Multiple Hearth Furnace
12 Explosives Switzerland	3/72	5	Nitrated Phenols	Equalization	150	Downflow Beds in Series	None
13 Pharmaceuticals Switzerland	10/72	25	Phenol	Equalization pH Adjustment Settling	60	Downflow Beds in Series	None
14 Insecticide England	1962		Chlorophenol	Equalization Clarification		Downflow Beds in Series	Rotary Kiln
15 Wood Chemicals Mississippi	8/73	3000	TOC	pH Adjustment Flotation Filtration	60	Moving Beds	Multiple Hearth Furnace
16 Dyestuffs Pennsylvania	8/73	1500	Color TOC	Equalization Clarification Filtration	50	Moving Beds	Multiple Hearth Furnace

Source: Ref. 11

TABLE 12

INDUSTRIAL WASTE ADSORPTION TREATMENT PLANTS USING CARBON

Location	Impurity	Average Flow Rate	Reactivation or Regeneration Method
Washington, N. J.	Polyols	100 gpm	Furnace
E. St. Louis, Illinois	Nitrophenol	50 gpm	Caustic
Burlington, Iowa	TNT	100 gpm	None
Southampton, Pa.	Dye	350 gpm	Furnace
Portland, Oregon	Insecticides	100 gpm	Furnace
Conway, N. C.	Phenol	25 gpm	Caustic
Wilmington, Cal.	Refinery Wastes	2900 gpm	Furnace
Latrobe, Pa.	Cyanide	20 gpm	None

Source: Ref. 35

ADSORPTION, RESIN

Prepared by

Warren J. Lyman

I. CONCLUSIONS AND RECOMMENDATIONS

Resin adsorption is a process which may be used to extract, and, if desired recover dissolved organic solutes from aqueous wastes. Ion exchange, a resin process for the separation of inorganic ions, is covered in another section of this report. The nature of the resin adsorption process is similar to carbon adsorption and the two processes may be competitive in several applications. The most significant difference between carbon and resin adsorption is that resins are always chemically regenerated (by use of caustic or organic solvents) while carbons, because the adsorption forces are stronger, must usually be thermally regenerated thus eliminating the possibility of material recovery. On the other hand, resins generally have a lower adsorption capacity than carbons.

Resin adsorption should be given serious consideration:

- For the treatment of highly colored* wastes; BOD and COD may be high;
- When material recovery is practical;
- Where selective adsorption is desired;
- Where low leakage rates are required;
- Where carbon regeneration is not practical; and,
- Where the waste stream contains high levels of dissolved inorganic solids.

Resin adsorption is not likely to be competitive with carbon for the treatment of high volume waste streams containing moderate to high concentrations of mixed wastes with no recovery value. A combination of resin and carbon adsorption may be attractive, however.

Relatively little information is available on the few systems that are currently in operation and thus there are areas of uncertainty concerning practicability, start-up problems, realistic operating costs, etc.

Neither environmental nor energy issues are of serious concern with this process.

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*"Color" here means the appearance of hue due to organic (and not inorganic) molecules.

II. PROCESS DESCRIPTION

A. BACKGROUND

Adsorption on synthetic resins is being considered here primarily as a process for the removal of organic chemicals from liquid waste streams; a separate report on ion-exchange resins, which are used for inorganic ion removal and/or recovery, appears elsewhere in this report.

While the earliest investigations of adsorption on synthetic resins date back to the mid-1940's, the technique has found its way into industrial use only in the last decade. The use of these resins is increasing at present as more becomes known about their capabilities and as a wider variety of resins are manufactured for separation purposes.

In many respects, adsorption on resins may be considered similar to adsorption on carbon; and thus more researchers are investigating both types of adsorbents when conducting treatability studies on industrial waste streams. A combination of both carbon and resin adsorption has been proposed as being particularly attractive in some situations; thus this alternative should be kept in mind.

There are relatively few waste treatment processes in operation today based on resin adsorption, and publicly available information about the experiences at these installations is extremely limited. Consequently, many questions relating to practicability and economics must remain unanswered for the present.

B. UNDERLYING PRINCIPLES

Waste treatment by resin adsorption involves two basic steps: (1) contacting the liquid waste stream with the resins and allowing the resins to adsorb the solutes from the solution; and, (2) subsequently regenerating the resins by removing the adsorbed chemicals, often effected by simply washing with the proper solvent.

The chemical nature of the various commercially available resins can be quite different; perhaps the most important variable in this respect is the degree of their hydrophilicity. The adsorption of a non-polar molecule on to a hydrophobic resin (e.g., a styrene-divinyl benzene based resin) results primarily from the effect of Van der Waal's forces. In other cases, other types of interactions such as dipole-dipole interaction and hydrogen bonding are also important. In a few cases, an ion-exchange mechanism may be involved; this is thought to be true, for example, in the adsorption of alkylbenzene sulfonates from aqueous solution on to weakly basic resins; e.g., a phenol-formaldehyde-amine based resin (Ref. 1).

While it is not possible to predict accurately the degree of adsorption that will take place in any case, it is a useful general concept that hydrophobic or nonpolar molecules (or portions of molecules) are attracted to hydrophobic surfaces, and that hydrophylic or polar molecules are attracted to hydrophylic surfaces.

An important aspect of resin adsorption is that the strength of the attractive forces between the solute molecules and the resin is usually weaker than that associated with adsorption on carbon. This allows for easier adsorbent regeneration along with improved potential for recovery of the adsorbed substances; with carbon, thermal regeneration is usually required and this does not allow solute recovery.

C. OPERATING CHARACTERISTICS

1. Feed Stream

The feed stream into a resin adsorption system must be a single liquid phase; in most cases this will be an aqueous solution, but there is no basic reason that an organic solution could not be treated so long as the resin is not chemically or physically harmed by the solution. Other limitations include the following:

a. Suspended Solids should be no higher than 50 ppm and may have to be kept below 10 ppm in some cases to prevent clogging of the resin bed.

b. pH may vary widely; some resins have been able to operate as low as pH 1-2 and as high as pH 11-12. In many cases, adsorption will be pH dependent, and will thus require pH control.

c. Temperature may also vary significantly. Resins have been used in applications where the influent temperature was as high as 80°C. Adsorption will, however, be favored by lower temperatures. Conversely, regeneration will be aided by higher temperatures.

d. High levels of Total Dissolved Solids (particularly inorganic salts) do not interfere with the action of resin adsorbents on organic solutes. There are clear indications that some organic chemicals are more easily removed from solutions with high concentrations of dissolved salts than from salt-free solutions. In some cases of high salt content, the adsorbent may have to be prerinsed before regeneration.

e. Concentration of Organic Solute(s) in the feed stream should probably be at least a factor of ten less than the maximum amount that can be adsorbed in a resin bed divided by three bed volumes;* this will allow a reasonably long cycle time. Higher influent concentrations may be treated if more frequent resin regeneration is acceptable. In the case of phenol adsorption, the upper limit on concentration is probably about 8% phenol by weight. There is no lower limit in concentration for resin adsorption, though it should be remembered that, as with carbon adsorption, adsorption is generally more efficient* at higher concentrations.

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*A "bed volume" is simply the volume of liquid required to fill a resin bed (i.e., container filled with resin beads).

f. Any chemicals, such as strong oxidants, which would chemically attack the resins must be kept out of the influent stream.

2. Process Operation

Resin adsorbents are used in much the same way as granular carbon. Commonly, a typical system for treating low volume waste streams will consist of two fixed beds of resin. One bed will be on-stream for adsorption while the second is being regenerated (see Figure 1). In cases where the adsorption time is very much longer than regeneration time (as might be when solute concentrations are very low), one resin bed plus a hold-up storage tank could suffice.

The adsorption bed is usually fed downflow at flow rates in the range of 0.25 to 2 gpm per cubic foot of resin; this is equivalent to 2-16 bed volumes/hr, and thus contact times are in the range of 3-30 minutes. Linear flow rates are in the range of 1-10 gpm/ft^2. Adsorption is stopped when the bed is fully loaded and/or the concentration in the effluent rises above a certain level.

Regeneration of the resin bed is performed *in situ* with basic, acidic, and salt solutions or regenerable non-aqueous solvents being most commonly used. Basic solutions may be used for the removal of weakly acidic solutes and acidic solutions for the removal of weakly basic solutes; hot water or steam could be used for volatile solutes; methanol and acetone are often used for the removal of non-ionic organic solutes. A prerinse and/or a postrinse with water will be required in some cases. As a rule, about three bed volumes of regenerant will be required for resin regeneration; as little as one-and-a-half bed volumes may suffice in certain applications.

Solvent regeneration will be required unless (1) the solute-laden solvent can be used as a feed stream in some industrial process at the plant (an example of such a situation is given in Section IV-C), or (2) the cost of the solvent is low enough so that it may be disposed of after a single use. Solvent recovery, usually by distillation, is thus most common when organic solvents are used. Distillation will, of course, allow solute recovery for reuse if such is desired.

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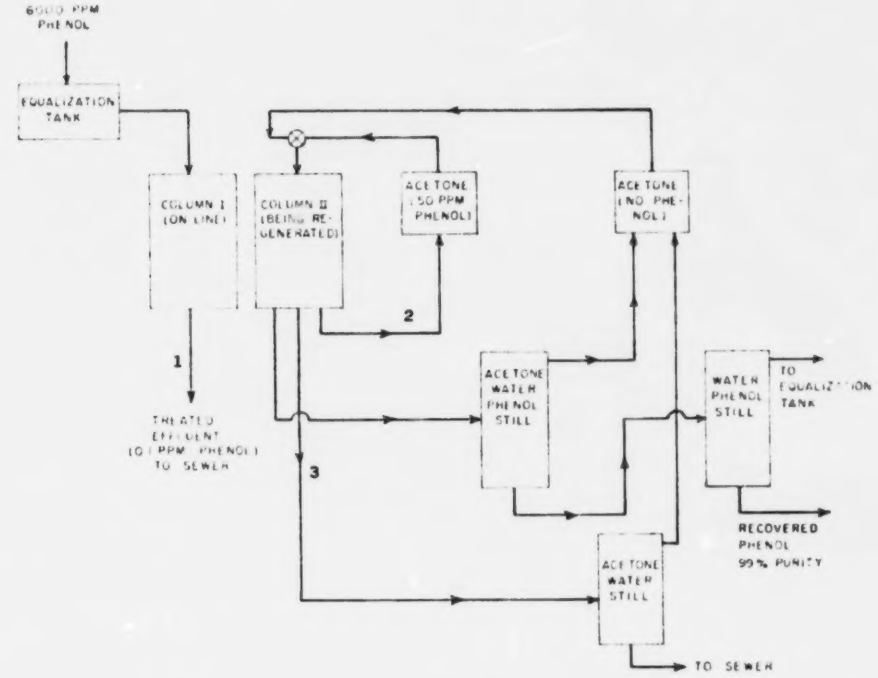
*i.e., the amount of solute adsorbed per unit weight of adsorbent will be higher.



Note: The three wash streams resulting from regeneration are sequential cuts, taken in the order listed. The last cut (#3) is a post rinse with water.

Source: Ref. 2.

FIGURE 1 **DIAGRAM OF A RESIN ADSORPTION SYSTEM FOR THE REMOVAL AND RECOVERY OF PHENOL FROM WATER**

Resin lifetimes may vary considerably depending on the nature of the feed and regenerant streams. Regeneration with caustic is estimated to cause a loss of 0.1 to 1% of the resin per cycle (Ref. 3); replacement of resins at such installations may be necessary every two to five years. Regeneration with hot water, steam, or organic solvent should not affect the resins, and in this case lifetimes will be limited by slow fouling or oxidation resulting in a loss of capacity; actual experience indicates that lifetimes of more than five years are obtainable.

3. Output Streams

Output streams from a resin adsorption system will vary from system to system. Details are given below.

a. Treated Effluent

All systems produce a treated effluent from which a significant portion of the organic solute(s) has been removed. If effluent guidelines or material recovery economics require a high degree of removal, this can usually be achieved by the proper adjustment of pH, flow, and contact time. In phenol removal (examples given in Section IV-C), the influent phenol concentrations of 1-5% are lowered to less than 10 ppm in the treated effluent. When a complex mixture of solutes is present in the influent, removal efficiencies may not be uniformly high.

b. Washing Effluents

Prerinse and/or postrinse of the resin bed (with water) is often required and will result in an aqueous effluent containing organic and/or inorganic solutes depending on the system. Treatment of these effluents will generally be required either for pollutant removal (before discharge) or for solvent recovery (as shown in Figure 1).

c. Regenerant Effluent

Each regeneration of a bed will result in about three bed volumes of regenerant effluent containing the solutes that had been washed off the resins. This effluent may:

1) be further treated for both solvent and solute recovery (as shown in Figure 1), in which case no significant effluents result,

2) be treated only for solvent recovery, e.g., by distillation, in which case a concentrated effluent would result from the still bottoms, or

3) be directly disposed of following any necessary treatment; in the case of caustic regeneration (typically 2-4% NaOH), evaporation followed by incineration may be used.

D. EQUIPMENT AND MATERIALS

Equipment needed for resin adsorption systems is relatively simple. The adsorption system will generally consist of two or more steel tanks (stainless or rubber-lined) with associated piping, pumps, and (perhaps) influent hold-up tank. Regeneration takes place in the same tanks, and thus the extra equipment needs for regeneration will consist only of such items as solvent storage tanks, associated solvent piping and pumps, and solvent (and perhaps solute) recovery equipment, e.g., a still. Up to three stills may be required in some systems such as the one shown in Figure 1.

Materials needed include a regenerant solution (e.g., aqueous caustic solution or organic solvent), and resin. In one full-scale installation for the removal of organic dye wastes from water (Refs. 4-7), two different resins are employed. In this case involving the waste stream is first contacted with a normal polymeric adsorbent and then with an anion exchange resin.

Features of a few currently available resin adsorbents are given in Table 1. Surface areas of resin adsorbents are generally in the range of 100-700 m^2/g; this is below the typical range for activated carbons (800-1200 m^2/g) and, in general, indicates lower adsorptive capacities, although the chemical nature and pore structure of the resin may be more important factors. This has been demonstrated in one application relating to color removal (Ref. 8).

Tests should be run on several resins when evaluating a new application. Important properties are the degree of hydrophilicity and polarity, particle shape (granular versus spherical), size, porosity, and surface area.

It is frequently possible to "tailor" a resin for specific applications because much greater control over the chemical and surface nature can be achieved in resin production than in activated carbon manufacture. The cost of developing a totally new resin would be prohibitive for most applications, but minor modifications of currently available resins are often feasible.

Current prices of off-the-shelf resins are in the range of \$85-200 per cubic foot, or \$1-5 per pound, compared with a typical price of about \$0.50 per pound for granular activated carbon.

TABLE 1

PROPERTIES OF SOME COMMERCIALLY AVAILABLE RESIN ADSORBENTS

Name*	Base	Specific Gravity (wet)	Void Volume (%)	Particle Size (mesh)	Bulk Density (lb/cu ft)	Surface Area (m^2/g)	Average Pore Size (Å)
XAD-1	styrene-divinylbenzene	1.02	37	20-50	–	100	200
XAD-2	styrene-divinylbenzene	1.02	42	20-50	40-44	300	90
XAD-4	styrene-divinylbenzene	1.02	51	20-50	39	780	50
XAD-7	acrylic ester	1.05	55	20-50	41	450	90
XAD-8	acrylic ester	1.09	52	20-50	43	140	235
Dow XFS 4256**	styrene-divinylbenzene	–	40	+10	27	400	110
Dow XFS 4022	–	–	35	20-50	–	100	200
Dow XFS 4257	–	–	40	20-50	–	400	110
Duolite S-30	phenol-formaldehyde***	1.11	35	16-50	∿30	128	–
Duolite S-37	phenol-formaldehyde***	1.12	35-40	16-50	40	–	–
Duolote ES-561	phenol-formaldehyde***	1.12	35-40	18-50	40-45	–	–
Duolite A-7D	phenol-formaldehyde***	–	–	–	–	24	–
Duolite A-7		1.12	35-40	16-50	∿40	–	–

*XAD resins manufactured by Rohm and Haas Company; Dow XFS resins manufactured by Dow Chemical U.S. A; Duolite resins manufactured by Diamond Shamrock Chemical Company.

**This resin is designed for use in vapor phase adsorption applications.

***Functional groups such as phenolic hydroxyl groups, secondary and tertiary amines are present on the basic phenol-formaldehyde structure. Physical form of these resins is granular as opposed to a bead form for the other brands.

III. APPLICATIONS TO DATE

A. HISTORY OF USE*

Adsorption of organic chemicals on synthetic resins was first reported around 1945, but apparently little effort was made to commercialize the process until the 1960's. Some of the early work was done with ion exchange resins and probably was related, in part, to the growing awareness of the nature and extent of fouling of ion exchange resins by organic chemicals.

By the mid-1960's, enough information was available to generate serious interest in resin adsorbents for waste treatment. Some of the earliest government-sponsored studies were carried out at the University of California (Berkeley, California) starting in 1966 with funds from the Federal Water Pollution Control Administration (Refs. 9-11). One study looked at the reduction of COD, color, and odor in secondary municipal wastewater (Refs. 9-10) and the other (Ref. 11) looked at phenol adsorption. In the former, color and odor removal were found to be very good, but the COD removal efficiencies were not outstanding. The most promising system investigated consisted of a resin column followed by a carbon column (Ref. 10).

At about the same time, other investigators were also claiming good removal of both refractory organics and dissolved mineral solids from secondary municipal effluents with a weak-base anion exchange resin (Ref. 12).

A large number of the more recent studies on resin applications in wastewater treatment have focused on color removal (Refs. 4-8, 13-21) with several of these looking at general organic removal as well. Also of some interest has been the adsorption of phenols (Refs. 2, 22-24). Other investigations have looked at detergent adsorption (Refs. 25, 26), munitions wastewater treatment, e.g., TNT removal (Refs. 27, 28), fatty acids (Ref. 23), proteins and viruses (Ref. 29), dehydroabietic acid (Ref. 30), municipal effluents (Refs. 24, 31) and metals removal (Refs. 6, 32).

Attention has been focused recently on the use of synthetic resins in connection with water quality analyses (see, for example Refs. 33-38). Some of the results of these studies may be helpful in estimating the degree of adsorption that could be expected for organic chemicals present in low concentrations in wastewaters since the chemicals being analyzed were generally present in ppm concentrations.

At present, there is a significant amount of interest in vapor phase applications for resin adsorbents, and at least one resin has been investigated in this mode (Ref. 39).

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*A good historical review of the early work in this field is given in Ref. 9.

B. PRINCIPAL CURRENT APPLICATIONS

There is little publicly available information on current or proposed industrial applications of resin adsorption systems. Several current applications of resin adsorption, for which some information is available are discussed below.

1. Color Removal

A dual resin adsorption system being used to remove color associated with metal complexes and other organics from a 300,000 gpd waste stream from a dyestuff production plant (Refs. 4-7); color is reduced from an average of 75,000 to 500 APHA units on the Pt-Co scale, and COD is reduced from an average of 5,280,000 to 2,600 ppm (Ref. 4). The system also removes copper and chromium present in the influent waste stream both as salts and as organic chelates. While there have been some problems with this system, the effluent does meet the NPDES requirements.

Two large systems are also currently operating to remove colored pollutants (derived from lignin) from paper mill bleach plant effluents in Sweden (Refs. 19, 20) and in Japan. The Swedish plant, which produces 300 tons of pulp/day, installed its system about three years ago. The resin adsorption system removes 92-96% of the color (initially 30-40,000 Pt-Co units), 80-90% of the COD, and 40-60% of the BOD from the effluent of the caustic extraction stage in the bleach plant (Ref. 40). The system consists of three resin columns, each containing about 20 cubic meters of resin. The system in Japan is for a 420 metric ton/day pulp plant and consists of four resin columns, each with about 30 cubic meters of resin. In both cases, the resins are regenerated with a caustic wash followed by a reactivation with an acid stream (e.g., H_2SO_4). Plant equipment costs were $1-$1.5 million, and direct operating costs are in the range of $.30-$.60/1000 gallons.

Some resin adsorption units in operation are used to remove color in water supply systems; others are used to decolorize sugar, glycerol, wines, milk whey, pharmaceuticals, and similar products. One plant in Louisiana, removing color from an organic product stream, is said to have been in operation for eight years now without replacement of the initial resin charge.

2. Phenol Removal

One plant in Indiana currently uses a resin system to recover phenol from a waste stream. This unit has been operating for about nine months (as of March, 1976) and is said to be performing satisfactorily. A dual resin system is currently being installed at a coal liquefaction plant in West Virginia to remove phenol and high molecular weight polycyclic hydrocarbons from a 10 gpm waste stream; methanol will be used as the regenerant for the primary resin adsorbent.

3. Miscellaneous Applications

One resin adsorption system, in operation for five years, is removing fat from the wastewaters of a meat production plant. Other applications include the recovery of antibiotics from a fermentation broth, the removal of organics from brine*, and the removal of drugs from urine for subsequent analysis. Adsorbent resins are also currently being used on a commercial scale for screening out organic foulants prior to deionization in the production of extremely high purity water.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

There are several proposed resin adsorption systems.

1. Munitions Wastewater Treatment

Following recent investigations by the Army (see, for example, Refs. 27, 28) and the Navy, it is likely that full-scale resin adsorption units will soon be installed at two or three DOD installations. A decision to install such a system at the Naval Ammunition Depot in McAlister, Oklahoma, has reportedly been made, and a system will probably be installed at the Milan Army Ammunition Plant. The Crane (Indiana) Naval Ammunition Depot is the third possibility.

Where resin adsorption systems are involved, they will be used to remove such contaminants as TNT, 2,4-DNT, RDX** and HMX*** from the wastewaters. TNT concentrations in the wastewaters are on the order of 100 ppm; effluent criteria require that less than 1 ppm be present. The proposed adsorption units (one for each munitions building) will probably use acetone as the regenerant. Distillation will be used for solvent recovery and the still bottoms will be incinerated.

An economic analysis of the proposed resin systems has indicated that the total operating cost should be less than that associated with current practice which involves the use of carbon on a throw-away (i.e., no regeneration) basis.

2. Pesticide Manufacture Wastewaters

As part of an EPA demonstration project, the Velsicol Chemical Corporation of Memphis, Tennessee, will soon start-up a demonstration resin adsorption unit to remove Endrin and similar compounds from plant wastewaters. The system will treat about 100

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*A consumer product, Gilcraft Biosorb, is available for a similar application; the resins are put in salt water aquariums to remove harmful organic chemicals that tend to build up in the tank.

**RDX is cyclotrimethylenetrinitramine.

***HMX is cyclotetramethylenetetranitramine gpm and reduce pesticide concentrations, present at up to 1 ppm in the influent (typically ~20 ppb), to less than 1ppb in the effluent. Isopropanol will be used for resin regeneration and distillation for solvent recovery; the still bottom will be incinerated.

In the latter part of 1976, another company is expected to start operation of a resin adsorption system for the treatment of wastewaters containing pesticides. No details are available for this system.

3. Carcinogen Removal

The National Center for Toxicological Research in Jefferson, Arkansas, plans to install a resin adsorption system by mid-1977 to remove trace levels of chemical carcinogens from their laboratory wastewaters. The resin system was chosen over carbon apparently because of the low leakage rate. The system will be designed for "zero" discharge of pollutants in a waste stream whose flow is about 100 gpm. Waste will flow from a holding tank through the resin bed at about 1 gpm/cu ft of resin. Because the influent concentrations are so low, the resin bed can theoretically run for years before regeneration would be required. Regeneration will, however, be carried out every few months using methanol. The used regenerant solution will all be incinerated. A 1 gpm pilot plant resin adsorption unit is currently in operation at the Center.

4. Phenols Removal

One chemical manufacturing plant in Kansas is currently investigating resin adsorbents for the removal of several phenolic compounds, including 2,4 dichlorophenol, from their wastewaters. Laboratory tests have been made and some resins have been found to be quite effective. A final decision has not been made about a full-scale system, but it is likely that a resin adsorption system will be a part of future wastewater treatment facilities at this plant. In the latter part of 1976, a second plant is expected to start operation of a new resin adsorption system for the treatment of phenolic wastes. No details are available for this system.

5. Wastes Containing Chlorinated Hydrocarbons

The Rohm and Haas Co. is currently preparing to commercialize a process to remove ethylene dichloride from vinyl chloride manufacturing wastewaters. Pilot plant work has been carried out. In this case the ethylene dichloride is removed from the resin with steam; steam requirements are reported to be much less than would be required for steam stripping.

D. POTENTIAL WASTE TREATMENT APPLICATIONS

Resin adsorption (excluding ion exchange with inorganic species) is expected to be applicable for the removal of (1) organic solutes from aqueous wastewaters, and (2) organic or inorganic solutes from non-aqueous liquid wastes, but the latter cannot be expected in the near term because so little has been done in these areas. Table 2 summarizes actual and potential waste treatment applications in a general way.

When aqueous waste streams are involved, resin adsorption may be considered particularly attractive in the following situations.

1. Treatment of Highly Colored Wastes

Resins have proven to be very efficient for color removal (primarily color associated with organic molecules) and to be capable of removing a significant fraction of COD and BOD at the same time.

2. For Material Recovery

When one or more solutes of commercial value are present in high enough concentrations to merit consideration of material recovery, resins should be considered since it is relatively easy to recover certain solutes following resin adsorption.

3. Where Selective Adsorption (and Perhaps Recovery) Is Wanted

Resins may be designed to be selective. For example, special resins may be made that will a) selectively remove aromatics from linear hydrocarbons (especially hydrophylic ones), b) selectively remove amines from other hydrocarbons, c) selectively remove weak organic acids from other hydrocarbons, and d) selectively remove macromolecules (e.g., dye bodies) from wastewaters containing other material.

TABLE 2

ACTUAL AND POTENTIAL WASTE TREATMENT APPLICATIONS OF RESIN ADSORPTION

I. Wastes that have been treated (pilot plant or commercial installation)

Physical Form	Hazardous Components	Component Concentration
Aqueous Solution	Phenols	High
	Color (plus some COD & BOD)	High
	Explosives (TNT, DNT, HMX, RDX)	Low
	Pesticides (e.g., endrin)	Low
	Fat	?
	Chemical Carcinogens	Very Low
	Chlorinated hydrocarbons (e.g., ethylene dichloride)	Low (?)

II. Wastes that may be treated

Physical Form	Hazardous Components	Component Concentration
1. Aqueous Solution	Almost any organic chemical	Low – High
2. Aqueous Solution	Some inorganic chemicals (?)	?
3. Non-Aqueous Solution	Some inorganic or organic chemicals (?)	?

4. Where Low Leakage Rates Are Required

In two studies (the removal from water of low levels of pesticides, and chemical carcinogens) resins were chosen, in part, because of the low leakage rate. This apparently results from rapid adsorption kinetics.

5. Where Carbon Regeneration Is Not Practical

If an adsorption process on a moderate-to-high-volume waste stream is desirable, and carbon could not be regenerated in such an application, then resin adsorption may be more economical; e.g., with munition plant wastewaters which contain explosives thermal regeneration of carbon is not safe, and chemical regeneration of carbon is not practical; thus carbon must be used on a throwaway basis.

6. Where the Waste Stream Contains High Levels of Inorganic Dissolved Solids

High levels of inorganic dissolved solids can pose problems for carbon adsorption systems. They may deposit on the carbon during thermal regeneration, and cause severe scaling, resulting in appreciable loss of activity. This is not a problem with resins which are not thermally regenerated, though they may require a prerinse with water before solvent regeneration.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements for resin adsorption systems are minor except where solvent and solute recovery via distillation are involved. In systems where distillation is not required, the energy requirements consist only of electricity for pumps, stirrers and controls and may only account for about 5% of the direct operating costs.

In the worst case, where both solvent and solute recovery are via distillation, up to three distillation columns may be needed (see, for example, the system shown in Figure 1). If, additionally, the influent solute concentration is high, frequent bed regeneration may be required and large quantities of steam will be used for the distillation columns. Electricity requirements will also be higher. In such a case, energy requirements may account for over half of the direct operating costs.

B. ENVIRONMENTAL IMPACTS

The only major environmental impacts resulting from the use of resin adsorption systems are related to the disposal of the used regenerant solution or the extracted solutes when they are not recycled. For example, when highly colored wastewaters are treated, the used regenerant solution (containing 2-4% caustic plus the eluted wastes) is not recycled and must be disposed of, usually by evaporation and incineration. A second example would be the removal of pesticides from water, with regeneration being effected by an organic solvent. In this case, the solvent would be recovered, probably by distillation, resulting in a concentrated waste (still bottoms) to be disposed of, probably by incineration. In both of these examples where incineration is used for the eventual destruction of the wastes, the environmental impacts would be on air quality (from incinerator emissions), energy use (for the incinerator fuel), and land use (from the disposal of unburned residues).

Only minor environmental impacts might be associated with the rinse waters discharged. In most cases, these effluents can be adequately treated by conventional means or safely discharged to surface waters.

Resin adsorption systems are relatively compact and thus require little space. The systems do not have any known health or safety problems associated with their operation.

C. ECONOMIC ANALYSIS

The costs of wastewater treatment by resin adsorption can very widely depending on the nature of waste being treated and the system design. As with carbon adsorption systems, two primary variables in the process economics are (1) the resin exhaustion rate (i.e., the amount of resin required to treat a given volume of liquid) and (2) the superficial liquid retention time (i.e., the time that the liquid takes to fill the volume of the resin bed). For a given flow, influent concentration, and resin, the capital and operating costs will depend almost entirely on these two variables. The operating costs are determined primarily by the resin exhaustion rate since this will set the frequency of regeneration required. The total capital costs will be determined primarily by the superficial liquid retention time since this will set the size (or number) of the resin beds required. Additional discussion on the relationship of these two primary variables to each other and to system costs is given in the report on carbon adsorption, found elsewhere in this report.

Some information is available on three significantly different types of waste streams:

1. Phenol recovery from concentrated waste streams,

2. Color removal from concentrated waste streams, and,

3. Pesticide removal from very dilute waste streams.

Treatment costs for these three types are given in subsections 1-3 below. Two detailed cost analyses are given for phenol recovery; in cases such as this where a valuable product is recovered in quantity, the waste treatment may be able to operate at a profit when credit for the recovered material is included. The two examples given show a profit, even though the total operating costs (before credits) are over $20/1000 gallons. The data cited for color and pesticide removal indicate total operating costs may be under $1/1000 gallons for such applications.

1. Phenol Recovery (two examples)*

a. Process for the Recovery of Phenol from Aqueous Streams: Acetone Regeneration System

This process is designed to remove and recover phenol from aqueous streams with phenol concentrations up to about 8% by weight. Other soluble constituents, such as inorganic salts, in the stream do not interfere with the process.

The effluent will meet environmental legislation or other standards requiring less than 10 ppm phenol. In many cases, less than 1 ppm phenol can be achieved.

Application of this AMBERLITE adsorption process is the treatment of effluent from plants manufacturing (1) phenol via cumene oxidation and (2) bisphenol A. Both of these processes use phenol and acetone.

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*The information for these two examples was supplied by the Rohm & Haas Company, Philadelphia, Pennsylvania. The cost estimates are, however, by ADL.

The recovery process, summarized in Figure 2, consists of three steps:

(1) Loading

(2) Regeneration and rinse, and,

(3) Distillation and separation.

(1) Loading – Adsorption is normally carried out on two columns, one of which is on-stream (i.e., being loaded) while the other is being regenerated. Loading is performed at a space velocity, (i.e., volumetric flow rate per volume of adsorbent) that is dependent on the phenol concentration of the influent, the desired effluent concentration, and on the time required to regenerate the unit.

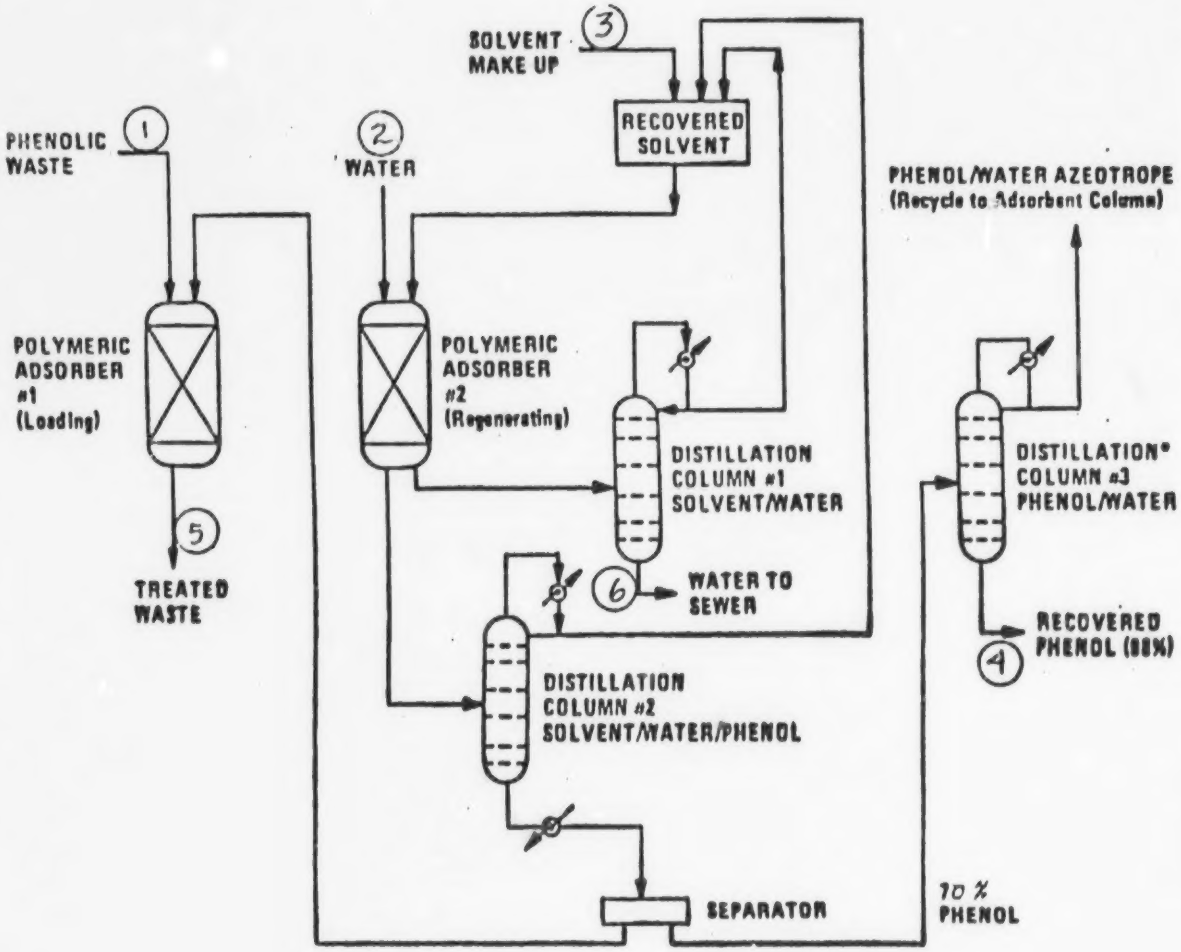
(2) Regeneration and Rinse – Acetone is used for regeneration, and is in turn displaced from the adsorbent by water or steam. The stream resulting from this operation is fractionated to optimize solvent recovery. The fractions containing the majority of acetone, the eluted phenol and mixed water are sent, in the case of cumene-phenol manufacture, to existing distillation facilities on site. A separate distillation unit may be required in the case of bisphenol A manufacture.

(3) Distillation and Separation – The distillation section permits acetone recovery at high purity, leaving water and phenol in the bottom of the column. Three distillation columns are shown in the flow sheet. In some situations, a single column can be used to achieve a 70-90% phenol product.

Usually, the concentration of recovered phenol in the eluate decreases as the concentration in the influent stream decreases. To counteract this problem and to minimize distillation costs, a novel variation of the process, called "superloading" can be used to maintain a high phenol-to-water ratio in the eluate, regardless of the influent concentration. This improvement is achieved by a separator (see Figure 2) which provides an organic phase containing 70% phenol and an aqueous phase saturated with phenol (about 7%). The latter can be recycled to "superload" the AMBERLITE adsorbent in a parallel bed.

(4) Licensing – The Rohm & Haas process for removal and recovery of phenol is covered by United States and foreign patents. A license may be obtained to practice the invention from Rohm & Haas.

(5) Costs – The capital and operating costs for this system are summarized in Table 3.


SOLVENT MAKE UP
③
RECOVERED SOLVENT
PHENOLIC WASTE
①
②
WATER
PHENOL/WATER AZEOTROPE (Recycle to Adsorbent Column)
POLYMERIC ADSORBER #1 (Loading)
POLYMERIC ADSORBER #2 (Regenerating)
DISTILLATION COLUMN #1 SOLVENT/WATER
DISTILLATION* COLUMN #3 PHENOL/WATER
⑤
TREATED WASTE
⑥
WATER TO SEWER
RECOVERED PHENOL (88%)
④
DISTILLATION COLUMN #2 SOLVENT/WATER/PHENOL
SEPARATOR
70 % PHENOL

COLUMN #3 UTILIZED WHEN HIGHLY PURE PHENOL IS REQUIRED

Material Balance, lbs/hr

	①	②	③	④	⑤ + ⑥
Phenol	264			264	< 10 ppm
Water	21,736	1480		9	23,207
Acetone			4		4
Total	22,000	1480	4	273	23,211

Source: Rohm and Haas Co., Philadelphia, Pa.

FIGURE 2 PHENOL REMOVAL AND RECOVERY SYSTEM – SOLVENT REGENERATION OF AMBERLITE ADSORBENT

TABLE 3

RESIN ADSORPTION SYSTEM COSTS: PHENOL RECOVERY – ACETONE REGENERATION

Basis: 525,000 lb/day of 1.2% Phenol in Water; 330 days/yr Operation; Recovered Phenol: 2.08×10^6 lb/yr.

Estimated Capital Investment: $780,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Labor	4,500 hrs	$12/hr	54,000
Maintenance (4% of Inv.)			31,000
Utilities			
Electric	150×10^3 kWh	$0.02/kWh	3,000
Steam	42×10^6 lb	\$4.00/10^3 lb	168,000
Cooling Water	250×10^6 gal	\$0.03/10^3 gal	8,000
Make-up Water	12.5×10^6 gal	\$0.40/10^3 gal	5,000
Total Utilities			184,000
Resin Replacement	100 cu ft	$140/cu ft	14,000
Acetone Replacement	35,000 lb	$0.15/lb	5,500
Royalty (0.5¢/lb phenol)			11,000
Total Variable Costs			$299,500
Fixed Costs			
Taxes and Insurance (2% Inv./yr)			15,600
Capital Recovery			126,900
Total Fixed Costs			$142,500
Total Costs			$442,000
Unit Cost – (¢/lb Phenol)*			21.3
Unit Cost – (\$/10^3 gallons)			21.30

*Current selling price of phenol is 26¢/lb; this would yield an annual credit of $540,800.

Source: Arthur D. Little, Inc., estimates.

b. Process for the Recovery of Phenol from Aqueous Streams: Formaldehyde Regeneration System.

This process is designed to remove and recover the phenol of up to 7% concentration normally found in the phenolic wastewater from the production of phenol-formaldehyde resins. It does not remove the associated formaldehyde or methanol. The effluent will meet environmental legislation or other standards requiring less than 50 ppm phenol in the treated effluent. A flow diagram and material balance for the system are given in Figure 3. Costs are summarized in Table 4.

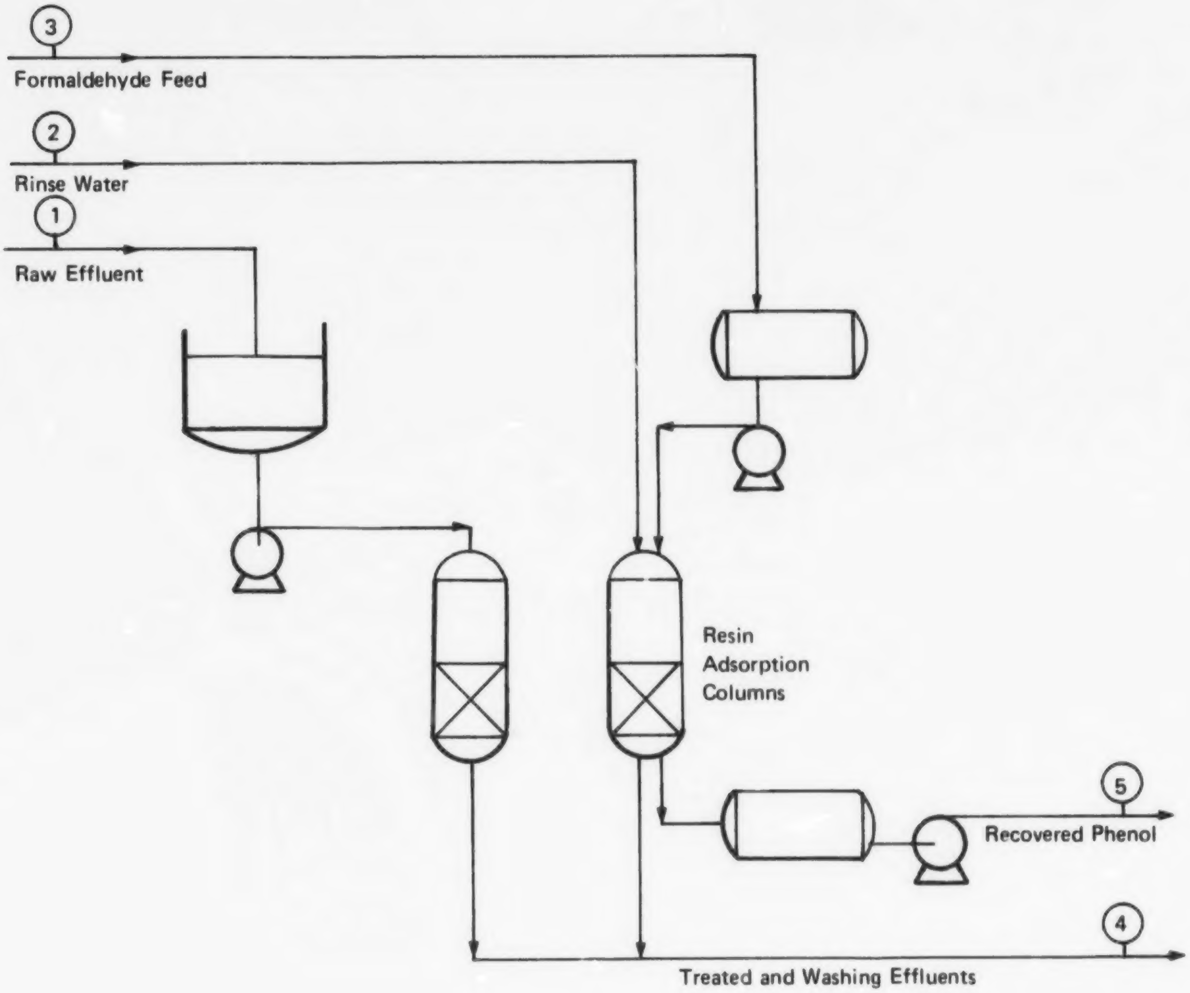
The main objective of this patented process is to eliminate the need for the capital and running costs associated with solvent recovery by distillation. Loading of the adsorption columns is carried out by the same procedure described for the acetone regenerated system. By the use of a 44% formaldehyde solution for regeneration, the process can recycle to the manufacturing process a regenerant eluate comprising a 37% formaldehyde solution containing the recovered phenol. As most phenol-formaldehyde resin producers normally use a 37% formaldehyde solution in their reactors, the regeneration costs are reduced to an absolute minimum.

2. Color Removal

The full-scale, three-column resin adsorption unit at the Swedish pulp mill required an initial investment of about $500,000 (Ref. 20). With an unbleached pulp of a Kappa No. of 35, the direct operating costs, excluding labor, were estimated (in 1974) to be as shown in Table 5.

If labor and capital depreciation had been included in the above example, net operating costs would probably be closer to $2/ton. Since a plant of this nature uses 10-15 tons of water per ton of pulp produced, the above figure may be translated into a total operating cost of about 50¢-80¢/1000 gallons. Other investigators have estimated the costs of removing color from a 800 ton/day pulp mill effluent to be as follows: capital costs, $920,000; total operating costs, $0.64/ton of pulp (Ref. 15).

In a hypothetical system designed to treat dye house wastes, it has been estimated (in 1974) that the fixed capital costs would be about $700,000, and direct operating costs about 25¢/1000 gallons (Ref. 4). This system would consist of three columns of polymeric adsorbents each followed by an anion exchange polisher, and would be capable of treating 500,000 gal/day.



Material Balance in lbs/hr

	①	②	③	④	⑤
Phenol	238			< 10 ppm	238
Water	4453	2781	2143	6768	2609
Formaldehyde	52		1714	73	1693
Methanol	19		39	21	37
Total	4762	2781	3896	6862	4577

Source: Rohm and Haas Co., Philadelphia, Pa.

FIGURE 3 PHENOL RECOVERY PROCESS – FORMALDEHYDE REGENERATION SYSTEM

TABLE 4

RESIN ADSORPTION SYSTEM COSTS: PHENOL RECOVERY – FORMALDEHYDE REGENERATION

Basis: 115,000 lb/day of 5% Phenol in Water; 330 days/yr Operation; Recovered Phenol: 1.9×10^6 lb/yr.

Estimated Capital Investment: $385,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Labor	3,000 hrs.	$12/hr	36,000
Maintenance (4% Inv.)			15,000
Electricity	200×10^3 kWh/hr	$0.02/kWh	4,000
Resin	50 cu ft	$140/cu ft	7,000
Formaldehyde (44%)	615×10^3 lb	$0.0555/lb	34,000
Royalty	2×10^6 lb	$0.005/lb	10,000
Total Variable Costs			$160,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			7,700
Capital Recovery (10 yr – 10%)			62,300
Total Fixed Costs			70,000
Total Costs			$176,000
Unit Costs (¢/lb of Phenol)*			9.3
Unit Costs ($/$10^3$ gallons)			38.60

*Current selling price of phenol is 26¢/lb; this would yield an annual credit of $494,000.

Source: Arthur D. Little, Inc., estimates.

TABLE 5

DIRECT OPERATING COSTS FOR COLOR REMOVAL FROM PULP MILL EFFLUENTS BY RESIN ADSORPTION

	$/Ton of Air Dry Pulp
Chemicals	1.26
Resin Refill (20%/yr)	.30
Electricity	.02
Total	$1.58
Credit for Salt Cake	.36
Credit for Steam Generated	.22
Total Credits	$0.58
Net Operating Costs = $1.58 – .58 =	$1/ton

Source: Ref. 20.

Color removal from surface waters (containing relatively small amounts of color bodies) has been estimated (in 1968) to cost about 2¢-4¢/1000 gallons (Ref. 13).

3. Pesticide Removal

In a study of the feasibility of treating the effluent from a pesticides manufacturing facility, a cost comparison for carbon and resin adsorption was made (Ref. 25). The data (from 1973) are summarized in Table 6 below.

TABLE 6

TREATMENT OF A WASTE STREAM ARISING FROM THE MANUFACTURE OF A CHLORINATED PESTICIDE

Influent: 200 ppm total chlorinated pesticides, pH 1.0, 150,000 gpd, run to 1 ppm leakage

	Treatment with Granular Activated Carbon	Treatment with Resin Adsorbent
Capital Investment (uninstalled)	$175,800	$99,500
Operating Expenses*	$ 73,000/yr	$45,150/yr
Total Operating Costs*	$1.33/1000 gal	$0.83/1000 gal

*Includes equipment depreciation (10-year life)

Source: Ref. 25.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

There are few data available on long-term effectiveness and reliability of resin adsorption systems (due to the fact that few full-scale systems are in use and information on experiences at these facilities is limited).

Resin adsorption systems for the removal of organic solutes from aqueous waste streams can be particularly attractive (as described in Section III-C):

- For the treatment of highly colored wastes (i.e., removal of organic color bodies);
- For the recovery of material (when one, or only a few, solutes are present in sufficiently high concentration to justify the costs of such treatment);
- Where selective removal of one substance, or a class of substances is desired;
- Where low leakage rates are required;
- Where carbon regeneration is not practical; and,
- Where the waste stream contains high levels of dissolved inorganic solids.

Most of these applications take advantage of some of the best features of resin adsorbents which include (1) the potential for chemical selectivity; (2) rapid adsorption kinetics; and, (3) efficient chemical regeneration.

The principal disadvantages of the process are associated with the following:

- Generally lower adsorption capacity than activated carbon (surface areas are smaller).
- Susceptibility to certain poisons such as oxidants or organic foulants that are not efficiently removed by the regenerant;
- The necessity of keeping suspended solids in the influent low enough to prevent clogging in the bed; and,
- The relatively high cost of the resins ($1-$4/lb) versus cost for activated carbon (about $.50/lb).

The cost comparison with carbon will be unfavorable to synthetic resins when both can be chemically regenerated. In situations where carbon must be thermally regenerated, the added costs of such regeneration may offset the lower cost of the adsorbent because of high losses of carbon, typically 4-9% per regeneration.

Resin adsorption systems would not normally be economically competitive with carbon systems for high volume waste streams containing moderate to high concentrations of mixed wastes with no recovery value. Such streams would include municipal and combined industrial effluents. A combination of resin and carbon adsorption may, however, be attractive.

Future developments may improve the attractiveness of resin adsorption in two ways. First, new resins may become available that will show improved performance (higher capacity and better selectivity). Second, increased use of such systems, along with increased competition for the sale of resins, may result in lower resin prices.

It is recommended that resin adsorption be given serious consideration for any waste stream with characteristics similar to those described above. The process will generally be in competition with activated carbon and may prove to be a viable alternative in some cases.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD (PARTIAL LISTING)

1. Bruce W. Stevens, Chester R. Fox and Evan H. Crook, Rohm & Haas Company, Philadelphia, Pennsylvania (company manufactures adsorbent resins and designs systems to use them).

2. Stephen E. Mehlberg, Dow Chemical U.S.A., Midland, Michigan (company manufactures adsorbent resins and designs systems to use them).

3. Dr. Irving M. Abrams, Diamond Shamrock Chemical Company, Redwood City, California (company manufactures adsorbent resins).

4. Anthony E. Perotti and Edward L. Shunney, Facet Enterprises, Inc., Warwick, Rhode Island (company includes the Waste Treatment Division formerly owned by Fram Corporation; the company developed Dualsorb® process for treatment of wastes with adsorbent resins).

5. Joe Phillips, Kamyr, Inc., Hudson Falls, New York (company has installed a resin adsorption unit at a pulp mill in Japan to remove color from wastewaters).

6. Professor Vernon L. Snoeyink, Department of Civil Engineering, University of Illinois, Urbana, Illinois (Dr. Snoeyink is an independent researcher and author of several papers in the area of resin adsorption).

7. Dr. Robert Andren, U.S. Army, Natick Research and Development Command, Natick, Massachusetts (Dr. Andren has carried out research and published papers on the use of resin adsorbents for treating munitions wastewaters).

8. Robert D. Fox, Hydroscience, Knoxville, Tenneseee (company consults in the area of waste treatment applications, including assessments of resin adsorption systems).

9. Terry Dillman, Illinois Water Treatment Company, Rockford, Illinois (company designs and installs waste treatment equipment including resin adsorption systems).

10. Dan Marx, Velsicol Chemical Company, Memphis, Tennessee (company is installing a demonstration resin adsorption system for the removal of chlorinated pesticides; project is primarily funded by EPA).

11. Dr. David Oestreich, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (Dr. Oestreich is the project officer on the Velsicol demonstration project mentioned in #10.)

12. A.H. Noble, Jr., ICI United States, Inc., Dighton, Massachusetts (Noble is the plant manager at this plant which uses a resin adsorption system for color removal from plant wastewaters).

13. Dr. David C. Kennedy, Ryckman-Edgerly-Tomlinson Associates, St. Louis, Missouri (company is developing a resin adsorption system to remove low levels of chemical carcinogens from laboratory wastewaters).

BIOLOGICAL TREATMENT: OVERVIEW

Prepared by

Sandra L. Johnson

I. CONCLUSIONS AND RECOMMENDATIONS

Biological treatment processes involve placing a waste stream in contact with a mixture of microorganisms, so that the organic compounds in the waste stream are decomposed. Typically, the microorganisms used in the process are present in the influent waste stream. The process optimizes the microbial environment, so that natural degradation is enhanced. Methods for optimizing biological degradation include controlling the dissolved oxygen level, adding nutrients, increasing the concentration of microorganisms, and slowly increasing influent waste concentrations so that an acclimated microbial population develops within the process.

Biological treatment is applicable to aqueous waste streams with organic contaminants. The organics may be either solvent or solid in the influent waste stream to be amenable to biodegradation. Water is essential in the waste stream. The microorganisms rely on enzymes to catalyze organic decomposition reactions, and the enzymes require water to remain active. In aerobic biological treatment processes, both simple and complex organics can eventually be decomposed to carbon dioxide and water. Oxygen is essential to the decomposition of long chain and aromatic hydrocarbons. In anaerobic biological treatment processes, only simple organics such as carbohydrates, proteins, alcohols, and acids can be decomposed.

Biological treatment processes do not alter or destroy inorganics. In fact, concentrations of soluble inorganics should be kept low so that enzymatic activity is not inhibited. Trace concentrations of inorganics may be partially removed from the liquid waste stream during the biological treatment, because of adsorption onto the microbial cell coating. Typically, microorganisms have a net negative charge and are therefore able to perform cation exchange with metal ions in solution. Anionic species, such as chlorides and sulfates, are not affected by biological treatment.

With a properly acclimatized microbial population and adequate equalization preliminary treatment to ensure a uniform hydraulic flow and organic concentration, biological treatment is applicable to industrial processing wastes. For the treatment of organics in an aqueous medium, it is probably the most cost-effective treatment. Energy and chemical demands are low compared to other processes; however, land requirements are greater. As might be expected, biological treatment processes increase their energy demand as specific modifications require less land.

II. PROCESS DESCRIPTION

A. BACKGROUND

This is an assessment of biological treatment systems relative to their overall applicability to industrial processing waste streams which are not legally dischargable to air or water. Separate reports describe each of the biological treatment processes discussed in this overview and summarized in Table 1.

These processes are:

- enzyme treatment
- activated sludge
- trickling filter
- aerated lagoon
- waste stabilization pond
- anaerobic digestion, and
- composting

All of the above treatment processes, except enzyme treatment, depend on the natural functions of living microorganisms. Enzyme treatment is included in the list because enzymes are normally formulated from living cells. In the strict sense, however, they are chemical compounds whose molecule consists of specific proteins. Enzymes are noted for their catalytic behavior. Since microorganisms are essentially "bags of enzymes," enzymes participate in all metabolic processes, enhancing and controlling the course of these processes. Enzyme treatment, however, stands alone; the enzymes are used apart from the cells from which they are derived.

Because the biological systems (excluding enzyme treatment) listed above contain living organisms, they require specific ratios of carbon, macro-nutrients and micro-nutrients. Water is a necessary component of all living organisms and must, therefore, be a vital part of the biological waste treatment systems. The systems are affected by physical factors of habitat, temperature, light and movement; by chemical factors of pH, oxygen, salinity and metals; and by biotic factors involving the mix and interrelations of the organisms present. In summary, the microorganisms thrive best in a steady state of environmental conditions that ensures their growth and maximizes the biological decomposition of wastes. Alterations to their environment can occur, but these must occur at such a rate that organisms are allowed to acclimate.

B. UNDERLYING PRINCIPLES

Microorganisms are known for two biochemical processes involving energy transfer and together they describe metabolism: assimilation (anabolism) and dissimilation (catabolism). In assimilation, organisms synthesize organic compounds from CO_2, water and other components. The process is endothermic and primarily involves reduction. Dissimilation, on the

TABLE 1

OVERVIEW OF BIOLOGICAL TREATMENT PROCESSES

Biological Process	Principal Microbial Population	Optimum Temperature	Range In pH	% Solids in Waste Stream	Average Retention Time	Organic Decomposed	Estimated BOD Upper Limits Effectively Handled	Effluent	Residue	Energy Demand As % Total Cost	Chemical Demand As % Total Cost	Total Cost/ 1,000 Gallons
Enzyme Treatment	None	Mesophilic	1.5-9.5 Varies per enzyme	< 50%	Nil	All can be decomposed by a series of enzymes	No limit	CO_2 and water if complete treatment, otherwise intermediate decomposition products	None	< 10%	< 10%	Prohibitive production and immobilization cost
Activated Sludge Treatment	Aerobic Heterotrophic Bacteria	Mesophilic	6-8	< 1%	< 1 Day	All but oil, grease and halogenated aromatics, nitrogen compound	<10,000 mg/l	CO_2 and water, 5%-15% influent BOD remains	Biomass sludge	> 10%	> 10%	< $5
Trickling Filter	Aerobic Heterotrophic Bacteria	Mesophilic	6-8	< 1%	< 1 Day	All but oil, grease and halogenated aromatics, nitrogen compound	< 5,000 mg/l	CO_2 and water, 10-20% influent BOD remains	Biomass sludge	< 5%	> 10%	< $3
Aerated Lagoon	Aerobic Heterotrophic Bacteria and Facultative Anaerobic Heterotrophic Bacteria	Mesophilic	6-8	< 1%	2-7 days	All but oil, grease and halogenated aromatics, nitrogen compound	< 5,000 mg/l	CO_2 and water, 10-30% influent BOD remains	Biomass sludge	> 10%	> 10%	< $3
Waste Stabilization Pond	Aerobic Heterotrophic Bacteria and Autotrophic Algae	Mesophilic	6-8	<0.1%	3-6 Months	Mostly carbohydrates proteins, organic acids and alcohols	<100 mg/l	CO_2 and water, 10-40% influent BOD remains	None	< 5%	< 5%	< $2
Anaerobic Digestion	Obligate Anaerobic Heterotrophic Bacteria	Thermophilic	6.4-7.5	< 10%	2 Weeks	Mostly carbohydrates proteins, organic acids and alcohols	Not applicable	Mixed liquor of biomass and interstitial water; 40-50% influent volatile sludge solids remain	"Stabilized sludge	< 5%	< 5%	< $15
Composting	Aerobic Heterotrophic Bacteria and Facultative Anaerobic Heterotrophic Bacteria and Fungi	Mesophilic and Thermophilic	5-8.5	< 50%	3-6 Months	All organics, phosphorus compounds and nitrogen compounds	No limit	Leachate with soluble organics	None	< 5%	> 10%	< $30

other hand, is exothermic and primarily involves oxidation and hydrolysis. During dissimilation, organisms decompose organic compounds to CO_2 and water, or partially decompose organics to lower molecular weight organics, i.e., alcohols to aldehydes or acids.

The organisms which perform assimilation are autotrophic, while those which perform dissimilation are heterotrophic. Autotrophic organisms may assimilate photosynthetically using sunlight for their energy source, or chemosynthetically using the energy from chemical reactions wherein inorganic elements are oxidized. Heterotrophic organisms obtain their energy from the decomposition of organics.

For the most part, the biological systems prevalent in waste treatment are heterotrophic. They may coexist with other types of organisms and partially depend upon them. In the instance of waste stabilization ponds, the heterotrophic organisms obtain some of their oxygen from algae, as the algae photosynthesizes organics and releases oxygen. Nitrifying bacteria, which are present in activated sludge systems, are autotrophic and able to chemosynthesize nitrate from ammonia.

Heterotrophic organisms may be either aerobes, obligate anaerobes, or facultative anaerobes. Aerobes require molecular oxygen for their respiration and synthesis; obligate anaerobes require the complete absence of oxygen, while facultative anaerobes obtain their energy for growth either in the presence or absence of oxygen. Aerobic synthesis proceeds faster than anaerobic synthesis and has a higher growth yield of cells resulting in more biomass sludge residual.

All of the biological systems require carbon as a food source. Some organisms are able to utilize a wide range of organic substances as their primary food source, while others are more specific. All microorganisms require certain ratios of nutrients. The essential macronutrients are nitrogen, phosphorus, sulfur, potassium, calcium, and magnesium. These are so-called macro-elements because of the quantity in which they are required. Micro-nutrients are just as essential as the macro-nutrients, but they are needed only in trace amounts. Micro-nutrients essential for growth include, for example, iron, boron, copper, manganese, zinc, chromium, and cobalt.

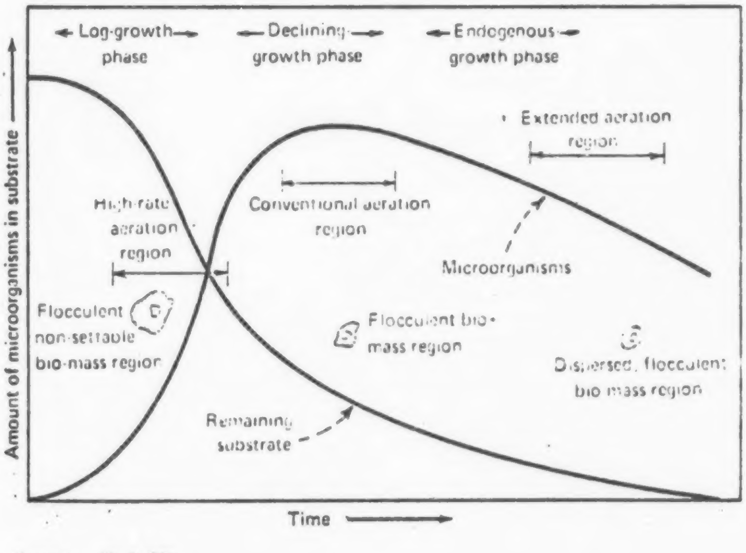
Water is the medium of life for microorganisms. The organisms synthesize water-soluble organics. Water is also an indispensable factor of plant life in temperature control, nutrient solvent, maintenance of correct pH values, control of osmotic pressure, hydrolysis reaction, oxidation reactions, and transport of ions and compounds.

Activated sludge, trickling filter and aerated lagoon treatment typically process wastewaters with less than 1% solids. Waste stabilization ponds process wastewaters with less than 0.1% solids. Anaerobic digestion normally operates on sludges with less than 10% solids; and composting operates on sludges of less than 50% solids.

C. OPERATING CHARACTERISTICS

Biological waste treatment systems vary primarily by the type of organisms present within the system (heterotrophic, autotrophic) and their mode of respiration and synthesis (aerobic, anaerobic, facultative anaerobic). The engineered systems which house the organisms can take a variety of forms designed to enhance the rate and efficiency of biological decomposition of wastes. Differences among the systems include: shape and size of the facility, media to support the organisms, flow rate and retention time within the facility, mixing or recirculation within the facility, addition of oxygen and/or heat into the biological system.

Biological treatment processes require a uniform range of flow, composition, and concentration. The retention time and the organic substrate to microorganism ratio determines the organics concentration levels which can be decomposed. As the waste substrate is introduced to the biological systems, microorganisms grow at a logarithmic rate (see Figure 1). As the substrate becomes limited, the growth rate declines and some microorganisms die. The dead microorganisms then become substrate for the remaining population. As the substrate continually decreases, the microorganisms metabolize the polysaccharide slime layer which coats their cell walls, resulting in denser and heavier cells. There is an optimum point at which the slime layer still exists and the organisms are fairly dense. At this point, if the organisms collide, they agglomerate and settle. However, if the substrate is so minimal that the slime layer has decreased to the point where there is no adhesion, so-called the endogenous growth phase, the individual particles do not agglomerate. Activated sludge treatment and trickling filters rely on the biomass retaining their slimy coating, and are therefore best operated in the log-growth phase. Aerated lagoons and waste stabilization ponds have long retention periods and exhibit endogenous growth. Compost and anaerobic digestion also exhibit endogenous microbial growth.



Source: Ref. 36.

FIGURE 1 BACTERIAL GROWTH AND SUBSTRATE CONSUMPTION

Microorganisms are poilikotherms, meaning that their body temperature is at or near the temperature of the medium in which they exist; therefore, their survival, reproduction, growth, and behavior are highly temperature dependent. Microorganisms have a range of temperature in which they achieve optimum growth. Temperature ranges for psychrophilic organisms are 0°C to 20°C, ranges for mesophilic organisms are from 20°C to 45°C, and ranges for thermophilic microorganisms go above 45°C. Temperature shifts in the influent waste to a biological system can cause shifts in the predominance of specific microorganisms within the mixed culture, and cause adaptation of certain microorganisms to the temperature effects and alterations in their metabolic processes. In an aqueous solution as temperature increases, dissolved oxygen levels generally decrease and the respiration rate of aerobic microorganisms is inhibited. Generally, impacts from temperature changes are less in a mixed biological culture than in a culture having a single organism.

Studies have indicated that the water-oriented biological treatment processes (activated sludge, aerated lagoon, waste stabilization pond, trickling filter and enzyme treatment) function best in a mesophilic range, while the digestion and compost systems which operate on more concentrated wastes function best in the thermophilic range. Once a system has organisms within a specific phase, i.e., mesophilic or thermophilic, it is important that the temperature changes are gradual. Generally, the temperature of the wastewater or the sludge is the controlling factor, rather than the temperature of the air. This is true as long as the hydraulic loading is sufficient and the system is relatively well contained.

Most organisms function within a relatively neutral pH range between 6 and 8. Some microorganisms are more sensitive to pH than others. In composting, the initial pH can be as low as 5 in the first 2 or 3 days. It then begins to rise and levels off at about 8.5 for as long as aerobic conditions are maintained (Ref. 30). On the other hand, methane bacteria present in anaerobic digestion systems flourish within a very narrow pH range of 6.4 to 7.5 (Ref. 27). Often pretreatment of wastes prior to aqueous biological systems includes pH control.

Metals inhibition varies with different biological species. Generally, toxicity takes the form of enzyme inhibition. A pure culture with a simple substrate may indicate a different behavior than a heterogeneous system of microorganisms will demonstrate. For example, a heterogenic culture in an actual activated sludge system is likely to demonstrate a mixed pattern of enzyme inhibition because of the multiple enzyme systems present. Metals are inhibiting when they are in solution. Controlling pH levels and encouraging formation of metal precipitates minimized inhibition.

D. EQUIPMENT AND MATERIALS

Biological treatment facilities rely on fairly simple equipment and materials. The microbiology of the systems is complex, and not completely understood; however, the systems to house the microbial populations are typically little more than open or closed concrete tanks of various shapes and sizes. Within the tanks, process modifications may include equipment for mixing, aerating, and circulating the microorganisms. Certain wastes may require the addition of alkaline chemical compounds to maintain neutral pH levels, and nutrients to maintain microbial activity.

All biological treatment processes, except perhaps the compost treatment system, are sensitive to variation in influent waste streams. As a result, equalization of industrial processing wastes should be provided prior to biological treatment. The equalization process generally involves a large holding basin where influent streams are allowed to mix to attain a steady-state waste stream of relatively uniform flow rate and composition.

Some of the biological systems provide media for support of microbial growth. Rock or synthetic plastic media is used to support biomass in the trickling filter system. Carbon is sometimes added to activated sludge systems to provide organic matrix and adsorptive capacity for inorganics. Compost systems rely on soil, wood chips, pulverized limestone, manure, etc., as media for microbial growth.

III. APPLICATIONS TO DATE

Biological treatment is applicable to aqueous waste streams with organic contaminants. Aerobic biological treatment systems can destroy all types of organics, while anaerobic biological treatment can perform only on simple organics such as carbohydrates, proteins, alcohols, and acids. Destruction of long chain and aromatic hydrocarbons requires incorporating molecular oxygen into the organic compound, and anaerobic organisms do not have the appropriate enzymes or environment to accomplish this oxidation mechanism.

Biological treatment does not decompose metal compounds. To some degree, metals are adsorbed onto the microbial population. Since the microorganisms tend to have a net negative charge, they provide cation exchange capacity for trace amounts of certain metal species. However, the concentration of soluble metals must remain low (generally less than a few milligrams per liter) to avoid inhibition of microbial growth.

Certain inorganic compounds may be treated using microorganisms, although the information on application is limited. Ammonia can be converted to nitrite and nitrate, and then to nitrogen gas through a controlled sequence of aerobic and anaerobic biological treatment steps. Phosphorus can be concentrated in microorganisms under aerobic conditions, then released under anaerobic conditions.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy demands for biological treatment vary by process. In waste stabilization ponds, energy requirements are for pumping of influent and effluent waste streams to and from the process. Energy requirements for trickling filters are for pumping, dosing, and wastewater recirculation. For the activated sludge treatment and aerated lagoon treatment processes, energy demands are from pumping, mixing, and aeration of the waste stream-microorganism mixed liquor. Anaerobic digestion requires energy to pump, mix, heat, and recirculate the waste stream. Composting energy requirements are for pumping, dosing and heavy equipment (dozer/shovel earth moving machine).

Chemical requirements for biological processes are limited. Chemicals may be needed for pH adjustment, metals precipitation, and/or nutrient additions. In systems operating on a uniform waste stream with sufficient biodegradable organic substrate and neutral pH, need for any chemical additives such as nitrogen and phosphorus varies according to the waste origin.

B. ENVIRONMENTAL IMPACTS

Environmental impacts associated with biological treatment processes are limited. There appear to be no exotic compounds formed in aerobic biological systems. In anaerobic systems, methane bacteria may transfer methyl groups to mercury or arsenate receptors. The gas emissions from the biological systems are carbon dioxide and nitrogen; and, under anaerobic conditions, methane. Solid emissions are biomass sludges, consisting of spent microorganisms with some accumulation of non-biodegradable inorganics and refractory organics. The liquid effluent of biological treatment contains some dissolved inorganics, and those soluble organics which have not been decomposed by microbial activity.

C. ECONOMIC ANALYSIS

The costs of biological treatment vary for the type and scale of process and the influent-effluent organic concentrations used as a design basis. Total costs vary from 5¢ to more than $15 per 1,000 gallons of influent waste. Generally, the costs increase as the influent organic concentrations increase and longer retention times are required. Waste stabilization ponds, for example, handle the most dilute waste streams of the biological processes considered. Total waste stabilization pond treatment costs range from about 5¢ per 1,000 gallons for a very dilute waste stream of less than 50 ppm BOD handled in earth-constructed ponds, to nearly $1.50 per 1,000 gallons for a waste stream of about 300 ppm BOD handled in ponds with plastic lining. Activated sludge treatment can accept waste streams of higher organic loading utilizing lower retention times because there is designed control of the level of dissolved oxygen and the concentration of microorganisms in the system. Total costs for activated sludge treatment range from about 20¢ per 1,000 gallons for a waste stream of about 300 ppm BOD, to nearly $2 per 1,000 gallons for a waste stream of about 4,000 ppm

BOD. Anaerobic digestion handles more concentrated waste streams than the above processes; total cost for digesting an organic waste of about 5% solids content is about $11 per 1,000 gallons of influent. Composting handles the most concentrated waste streams (up to 50% solids content) and requires the longest retention periods. The total cost for composting a waste stream of about 5% solids content is about $30 per 1,000 gallons. Since this report is concerned with industrial processing wastes, often a highly variable composition, the above costs include equalization and neutralization prior to biological treatment.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

In general, biological treatment processes are probably the most cost-effective techniques for treating aqueous waste streams containing organic contaminants. In order to be useful in industrial waste treatment, fairly uniform influents to the biological processes must be maintained. Therefore, biological processes should generally be preceded by neutralization and equalization facilities. Since soluble inorganics are inhibitory to microbial activity, preliminary treatment should be employed to lower the levels of these toxicants to threshold concentrations tolerated by acclimated microorganisms present in various processes.

Of the four biological wastewater treatment processes (activated sludge, aerated lagoon, trickling filter, and waste stabilization pond), the activated sludge treatment system is best suited for handling industrial wastes with organic constituents. The system is the most compact of the four, and the continuous circulation of biomass (activated sludge) allows development of an acclimated microbial population. The activated sludge system, especially pure oxygen process modifications, allows the greatest control of dissolved oxygen levels so that variable organic loadings can be accommodated without the system becoming oxygen-deficient.

The anaerobic digestion process is not well suited for industrial waste treatment of varying influent compositions. The process is not able to treat complex hydrocarbons, including long chain and aromatic compounds. Also, the microbial population contains highly sensitive methane bacteria, which cannot tolerate fluctuations in influent organic levels.

The composting treatment process employs long retention periods to decompose very high organic loadings. It is the optimum biological process for treatment of semi-solid industrial wastes of variable composition and concentration. Nearly all types of organic compounds are eventually biodegradable, although halogenated aromatic hydrocarbons may inhibit the microbial population.

Enzyme treatment has no potential for the variable industrial waste streams being considered here. The technique has potential only if there are significant quantities of one organic substrate such that resource recovery can be employed, i.e., municipal trash has sufficient cellulose to realize recovery of glucose through enzyme treatment.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD (Partial Listing)

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BIOLOGICAL TREATMENT: ACTIVATED SLUDGE

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I. CONCLUSIONS AND RECOMMENDATIONS

The activated sludge process is a well-developed treatment technology for the decomposition of organics in aqueous waste streams (less than 1% suspended solids). Pretreatment with lime of incoming waste stream is almost always necessary to remove heavy metals.

Activated sludge treatment is used extensively in industry, including at least two industrial waste treatment facilities. It is probably the most cost-effective manner of destroying organics present in an aqueous waste stream. By using activated sludge modes which ensure complete mixing and high dissolved oxygen levels, high strength organic waste streams can be handled at an industrial waste treatment facility.

II. PROCESS DESCRIPTION

A. BACKGROUND

The activated sludge process treats aqueous organic waste streams having less than 1% suspended solids content. In general the process is unsuited for slurries, solids, tars, or viscous waste streams. The process is described as having flocculated, biological growths which are continuously circulated and contacted with organic wastewater in the presence of oxygen. The process was patented in England about the turn of this century, and has steadily undergone modification and development. Much of the process modification has involved improved methods of maintaining aerobic conditions under varying organic loadings.

B. UNDERLYING PRINCIPLES

The activated sludge process relies on continuous recycle of living microorganisms (biomass) acclimated to the wastewater environment. The recycled biomass is a mixed culture of aerobic heterotrophic bacteria which decompose organic matter. The presence of fungi is not significant to the process. Protozoa and rotifers reside within activated sludge systems by feeding on the bacteria. Since the protozoa and rotifers are strict aerobes and sensitive to toxicants, operation monitoring of activated sludge systems includes routine microscopic observations of the mixed liquor for their presense as a sign of healthy activated sludge activity (Ref. 100).

Bacteria in activated sludge systems can be thought of as "bags of enzymes" capable of performing hydrolysis and oxidation reactions. Complex hydrocarbons are oxidized to lower molecular weights by oxygenase enzymes which incorporate oxygen directly into the long chain or cyclic hydrocarbon molecule (Ref. 74). Polysaccharides, fats, and proteins are degraded from their polymeric state to monomeric units via hydrolysis (Ref. 74). Both the oxidation of complex hydrocarbons and the hydrolysis of polysaccharides, etc. occur outside the cell, and are catalyzed by exoenzymes secreted from the cell wall into the surrounding aqueous environment. Oxidation is conducted by aerobic organisms which use dissolved oxygen present in the biological system. Hydrolytic reactions are caused by aerobic organisms using water present in the biological system.

The enzyme oxidation and hydrolysis reactions described above in the breakdown of large, i.e., generally more than 12 carton atom organics, into lower molecular weight organic compounds which can then pass through the cell wall (Ref. 100). The end-products which enter the cell, i.e., alcohols and acids, are metabolized by oxidation reactions catalyzed by endo-enzymes. The oxidation follows the chemical sequence of alcohols oxidized to aldehydes then to acids. A portion of the acids are oxidized to carbon dioxide and water to obtain the necessary energy to use remaining acids for cell growth.

Organics which can be decomposed by aerobic microorganisms include: polysaccharides, proteins, fats, alcohols, aldehydes, fatty acids, alkanes, alkenes, cycloalkanes, and aromatics (Ref. 74). Isoalkanes, halogenated hydrocarbons, and lignin are more resistant to microbial decomposition; however, decomposition does occur at a slower rate under appropriate conditions and with the right microbial population (Ref. 74). In Section III, the reported forms and levels of organics being treated by activated sludge are discussed. Aqueous feed streams with low (< 1%) solids having organic contaminants are applicable.

Not all of the organics removed from the wastewater influent are decomposed. For example, polychlorinated biphenyl (PCB) is known for its chemical stability and low biodegradability. Microorganisms do not naturally possess the enzymes necessary to decompose these synthetic organic compounds. PCB has been studied for its effects on the activated sludge treatment process (Ref. 136). Concentrations of PCB's up to 10 μg/l were added to acclimated and unacclimated activated sludge microbial systems. Oxygen uptake activity of sludge acclimated to PCB tended to be higher than the unacclimated sludge. The PCB was removed from the wastewater by concentration in the sludge biomass; however, no biodegradation of PCB was observed.

Metals present in concentrations nontoxic to bacteria in activated sludge systems are concentrated and separated by the treatment process. Most insoluble metals, i.e., metal oxides and hydroxides, are removed by sedimentation before activated sludge treatment. Dissolved metals and fine metal particulates are concentrated in the biomass, primarily through adsorption onto the activated sludge surface (Refs. 6, 7). It is suggested that the biomass surface is coated with a polysaccharide slime, consisting of polymers of glucuronic acid and neutral sugars (Ref. 135). Metal ions form salts with the carboxyl groups present in the slime coating and are electrostatically attached to the hydroxyl groups (Ref. 135).

In a study of cyanide removal by the activated sludge process it appeared that the extent of cyanide adsorption was related to the retention time of the sludge in the reactor (Ref. 140). The activated sludge was shown to adsorb appreciable amounts of soluble cyanide prior to progress of endogenous respiration. This might be expected with other metals because the endogenous growth period is characterized by deterioration of the polysaccharide slime coating (Ref. 36).

Most of the organisms in activated sludge systems are Gram-negative bacteria (Ref. 135). The biomass generally has a net negative charge. The polysaccharide slime coating the cells in the biomass is believed to contribute to the net negative charge. Activated sludge treatment, as a result, provides cation exchange capacity for positively charged metal species. Less concentration of anionic species is expected in the activated sludge system.

The State of Texas, with the assistance of Texas A&M University, studied trace metals removal by activated sludge treatment (Ref. 7). Their findings, averaged over a 4-month sampling period, are shown in Tables 1 and 2. The findings reported are strictly for the activated sludge process, and do not include additional metals removal which occurred in clarification steps preceding biological treatment. As shown, the percentage removal

TABLE 1

AVERAGE VALUES OF TOTAL HEAVY METAL CONCENTRATION

(4-Month Average)

DALLAS DEMONSTRATION PLANT

	Activated Sludge Influent mg/l	Activated Sludge Effluent mg/l
As	0.016	0.012
Ba	0.156	0.083
Cd	0.013	0.008
Cr	0.215	0.093
Cu	0.092	0.062
Fe	1.047	0.299
Hg	0.00051	0.00016
Mn	0.067	0.050
Ni	0.073	0.058
Pb	0.095	0.042
Se	0.0141	0.0028
Zn	0.320	0.112

Source: Ref. 7

TABLE 2

TOTAL HEAVY METAL REMOVAL EFFICIENCIES BY ACTIVATED SLUDGE TREATMENT

(4-Month Average)

DALLAS DEMONSTRATION PLANT

	Activated Sludge % Removal of Influent
As	25
Ba	47
Cd	39
Cr	57
Cu	33
Fe	72
Hg	69
Mn	25
Ni	21
Pb	56
Se	79
Zn	65

Source: Ref. 7

efficiency ranged from about 20-80%. The percentage removal of Hg, Se, Cd, Pb, Fe, Mn, and Zn correlated with influent concentrations; percentage removals increased as influent concentrations increased. On the other hand, percentage removals of As, Ba, and Ni decreased as influent concentrations increased.

In a study by the Washington State University, researchers found that arsenic is bioconcentrated through assimilation and adsorption (Ref. 50). They found a linear correlation existing between the concentration of arsenic in the influent and the concentration of arsenic in the biomass. For the amounts of arsenic studied, ranging from 0 to 156 μg/l, biota could concentrate arsenic in proportion to the amount available. See Table 3.

TABLE 3

ARSENIC REMOVAL BY BIOMASS

Washington State University Laboratory Study

Sample No.	Concentration, μg As/1 Influent	Effulent	In Activated Sludge Treatment Reduction of Arsenic %	Arsenic in Biomass μg As/g of Biomass
1	2.99	0.80	73	3.08
2	3.10	1.70	45	5.18
3	2.99	0.50	83	7.23
4	2.10	1.00	52	4.87
5	2.75	1.00	64	4.30
6	30.00	18.50	38	23.40
7	33.00	18.50	44	35.00
8	40.00	29.00	28	27.90
9	53.00	22.00	59	23.60
10	42.00	26.00	38	28.30
11	128.00	70.00	46	31.50
12	156.00	61.00	61	83.50
13	144.00	63.00	56	96.50
14	112.00	36.00	68	126.90
15	124.00	53.00	57	129.00

Source: Ref. 50

Researchers in Ontario studied the removal of metals by an activated sludge process receiving domestic-industrial wastewater (between 10-60% industrial). Their findings include both dissolved and total metals content. A large portion of the influent metals content to the activated sludge unit was dissolved, because much of the insoluble metals were removed by clarification processes prior to biological treatment. Their findings are presented in Tables 4 and 5. The tables indicate that metals are removed by adsorption of dissolved and fine particulate species onto the biological floc. All the metals removed are concentrated in the sludge, as shown in the last column of Table 5. There is no biological mechanism for the destruction of measurable quantities of metals compounds.

TABLE 4

MEAN VALUES OF TOTAL AND DISSOLVED HEAVY METAL CONCENTRATIONS OF 8-H

COMPOSITE SAMPLES

An Ontario Municipal-Industrial Treatment Plant

	Activated Sludge Influent		Activated Sludge Effluent		
Metal	Total ppm	Dissolved ppm	Total ppm	Dissolved ppm	Recycled Sludge ppm
Cd	0.003	< 0.001	0.001	<0.001	0.24
Cr	0.13	0.01	0.06	<0.01	9.72
Co	0.001	0.001	0.001	0.001	0.07
Cu	0.21	0.16	0.08	0.07	11.75
Fe	0.82	0.12	0.36	0.08	44.5
Pb	0.09	0.012	0.015	0.006	4.82
Mn	0.04	0.03	0.04	0.03	1.1
Hg	0.003	0.00003	<0.001	<0.00005	0.320
Ni	0.28	0.22	0.27	0.22	1.44
Zn	1.13	0.58	0.56	0.40	22.11

Source: Ref. 6

TABLE 5

THE EFFICIENCY OF HEAVY METAL REMOVAL

An Ontario Municipal-Industrial Plant

Metal	Activated Sludge Percentage Removal of Total Metals	Activated Sludge Apparent Percentage Removal of Dissolved Metals
Cd	50	–
Cr	54	70
Co	–	–
Cu	60	56
Fe	55	33
Pb	79	50
Mn	6	<1
Hg	<62	–
Ni	1	<1
Zn	50	30

Source: B.G. Oliver, E.G. Cosgrove, "The Efficiency of Heavy Metal Removal by a Conventional Activated Sludge Plant", Water Research, Vol. 8 pp. 869-874, Pergamon Press, 1974, Great Britain.

Metals can have an adverse effect on microbial metabolism because they inhibit enzyme catalysis. The metals affect enzymes by binding at the enzyme-active site or causing conformational changes in the enzyme (Ref. 142). Normally, microorganisms can tolerate only a few milligrams per liter of heavy metals (Ref. 100). There have been numerous studies on the inhibitory effect of metals on various microorganisms. The results are difficult to compare, as some researchers looked at metal inhibition on unacclimated cultures while others viewed acclimated cultures. In addition, the studies on pure cultures do not readily relate to the mixed population of microorganisms present in activated sludge systems. For example, *nitrosomonas* bacteria in a pure culture were reported inhibited by copper concentrations less than 1 mg/l, while *nitrosomonas* in mixed activated sludge required 4 mg/l of copper to produce the same level of inhibition (Ref. 94).

A study of separate bacteria and fungi cultures showed that toxic behavior of heavy metals is different for various biological species (Ref. 4). The metals were added in slug loads to unacclimated cultures. Silver and nickel were found less toxic to the *Geotrichum candidum* culture than to the *Zooglea ramigera* culture, while chromium, copper and zinc were more toxic to the *Geotrichum candidum* culture. When microorganisms are mixed together, a pattern of mixed inhibition can result and the tolerant species may predominate.

As the number of microorganisms in a given fluid volume increases, the adsorptive surface area for heavy metals removal increases (Ref. 100). This phenomenon has been observed in laboratory studies on copper toxicity, where the toxicity (indicated by glucose conversion) decreased as the number of microorganisms was increased (Ref. 94). Pure oxygen activated sludge systems, i.e., UNOX by Union Carbide, are reported to support higher concentrations of microorganisms than conventional activated sludge systems, thereby decreasing the toxicity effect associated with metals (Ref. 94). The so-called mixed liquor volatile suspended solids level (MLVSS) is believed a good indication of the quantity of active, viable organisms in the activated sludge. The pure oxygen systems have been shown to operate effectively at MLVSS concentrations of 4,000 to 8,000 mg/l, while conventional air activated sludge systems typically operate at 1,500 to 2,500 mg/l MLVSS (Ref. 138).

Certain refractory organics produce an inhibitory effect on activated sludge similar to metals inhibition. Some organic inhibitors alter the cell membrane permeability, preventing the organism from maintaining an appropriate environment for metabolism (Ref. 142). At levels of 1 ppm, 2, 4-dichlorophenol gives a characteristic metal-like inhibition demonstrated by decreased respiration (Ref. 133). For example, addition of 50 mg/l trinitrophenol seriously reduced activated sludge treatment removal efficiencies by inhibiting enzymatic activity. Adding 200 mg/l of trinitrophenol produced significant irreversible changes in the microbial activity (Ref. 5).

C. OPERATING CHARACTERISTICS

The process involves an aeration step followed by a sludge-liquid separation step, with recycle of a portion of the sludge. The basic system has an open tank for the mixture of the active biomass with influent wastewater and air, followed by a clarifier. A portion of the biomass, called activated sludge, is recycled to the open tank to maintain the food-to-mass (F:M) ratio (organic substrate-to-microorganism ratio). The conventional plug-flow system employs mixing wastewater and return sludge at the head of the aeration tank; the so-called mixed liquor flows through the tank in a plug-flow fashion with some longitudinal mixing. (See Figure 1.)

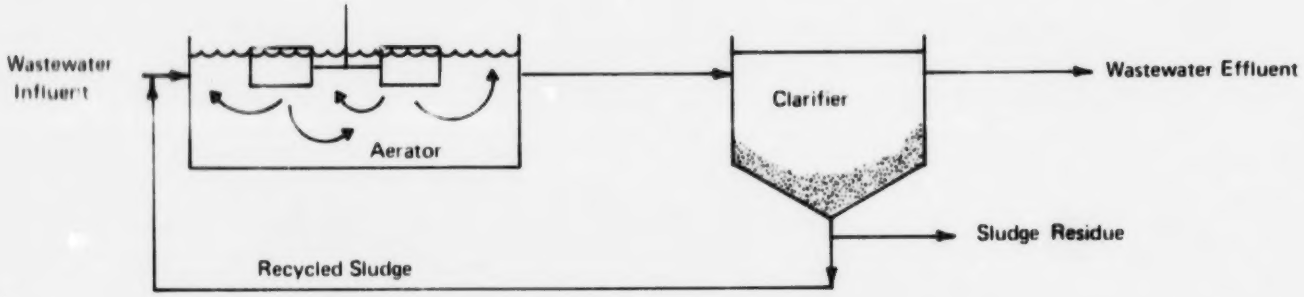

FIGURE 1 ACTIVATED SLUDGE SYSTEM

Process modifications of conventional activated sludge include the following:

- *Contact Stabilization* – used where BOD is rapidly removed from the aeration step by biosorption, and involves aerating the activated sludge on its return trip to the aeration tank so that sorbed organics are decomposed.
- *Step Aeration* – used to equalize influent organic loading along the course of flow of the mixed liquor, and involves admitting influent wastewater at multiple points along the aeration tank.
- *Completely Mixed* – used to equalize load variations and improve distribution of dissolved oxygen, and involves operating mechanical aerators in the aeration tank to achieve almost instantaneous distribution of untreated wastes throughout the tank.
- *Extended Aeration* – used where there are low organic loadings and it is desirable to minimize sludge residue, and involves longer aeration retention periods so that endogenous respiration of the biomass is achieved.

- *Pure Oxygen* – used where there are high organic and trace metals concentrations to maintain a high dissolved oxygen level and a high biomass concentration: and involves a closed staged aeration tank with mechanical mixers receiving concurrent flow of wastewater and oxygen gas.

Conventional activated sludge systems can not tolerate shock loadings of concentrated organics. Waste streams having significant variation in organic loading would require equalization in large basins prior to activated sludge treatment so as to be sufficiently uniform for treatment by acclimated microorganism. Activated sludge systems which operate with air or pure oxygen under pressure would be more able to withstand substantial influent variation (Refs. 95, 117, 118). The systems are closed reactors which automatically maintain dissolved oxygen concentrations of 5-10 mg/l in the mixed liquor (Ref. 137).

Microorganisms can acclimatize to moderately high dosages of metals if sufficient time is allowed to slowly increase concentrations. At a MLVSS concentration of 2,000 mg/l, mercury inhibition occurred at concentrations between 2.5-5 mg/l. However, even at mercury levels as high as 10 mg/l, recovery of the biological system occurred within several hours. The study found that the inhibitory effect of mercury was temporary, and the activated sludge system could acclimate to moderately high mercury levels if sufficient time was allowed (Ref. 14). When cultures of protozoa were acclimated with copper concentrations of 0.2 mg/l for 96 hours, their specific growth rate was 1.2 to 2.0 times as large when exposed to copper concentrations of 0.4 mg/l than the growth rate of protozoa receiving no acclimation (Ref. 1). Similarly, acclimatizing protozoa with chromium increased their specific growth rate 1.5 to 2.2 times that of nonacclimatized protozoa when exposed to chromium concentrations of 0.8 mg/l (Ref. 1).

Various researchers have reported threshold concentrations of metals to mixed activated sludge cultures. The threshold concentrations are limits of metals above which there is significant decrease in treatment efficiency (Ref. 141). Treatment efficiency measured by the Chemical Oxygen Demand (COD) of the effluent, enzymatic activity or the respiratory rate of the culture. In Table 6, Srinath (Ref. 94) presents a list of critical threshold metal concentrations based on review of available literature.

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TABLE 6

THRESHOLD CONCENTRATION FOR VARIOUS METALS IN THE AIR ACTIVATED SLUDGE PROCESS

Metal Ion	Concentration (mg/l)	Type A.S. Experiment
Silver	<.03	Carbonaceous
Vanadium	10.0	Carbonaceous
Zinc	2.0	Carbonaceous
	5-10	Carbonaceous
	1.0	Nitrification
Nickel	1.0-2.5	Carbonaceous
	1.0	Nitrification
	2.0	Nitrification
Chromium, $^{+6}$	10.0	Carbonaceous
	1.0	Nitrification
	10.0	Nitrification
	1.0	Nitrification
Chromium, $^{+3}$	10.0	Carbonaceous
Lead	10	Carbonaceous
Iron (Ferric)	15	Carbonaceous
Copper	1.0-10.0	Carbonaceous
	1.0	Nitrification
	2.0	Nitrification
Cadmium	1.0	Carbonaceous
	5.0	Nitrification

Source: Compiled by Dr. E.G. Srinath, Union Carbide, Tonawanda, N.Y., 1976.

III. APPLICATIONS TO DATE

A. CURRENT PRINCIPAL APPLICATIONS

The activated sludge process has been applied extensively to treat wastewaters from municipalities. Industrial applications include canneries (Refs. 32, 46), paper and pulp mills (Refs. 21, 32, 42, 43, 147), refineries (Refs. 32, 100), breweries (Ref. 146), steel plants (Ref. 32), textile plants (Ref. 32), petrochemical plants (Refs. 31, 143, 144), pharmaceutical plants (Ref. 95) and timber processing plants (Ref. 128).

Canneries have high biodegradable organic loadings, with BOD levels reported to 11,000 mg/l according to the product (Ref. 32). Pulp and paper mill wastes are characterized by high BOD levels (about 300-500 mg/l) and high COD levels (about 800-1,800 mg/l) (Refs. 32, 147). While high BOD removals are attained by activated sludge treatment of pulp and paper mill wastes, the COD levels are generally lowered by less than 50%. Wastewaters in the timber industry are reported to have 98% BOD removal, and 70 percent COD removal of influent steam process wastewater streams averaging 3,500 mg/l BOD and 8,450 mg/l COD. Tannins, pseudo-humic matter, phenols, polyphenols, certain pentosans and simple sugars disappear completely, leaving polysaccharide compounds (such as cellulose) in the effluent (Ref. 128).

A typical refinery waste contains oil, sulfides, and phenols (Ref. 31). Activated sludge treatment decomposes an average phenol loading of 135 mg/l by 85-95 percent. Oil compounds have been determined experimentally to not inhibit activated sludge culture. After a shock load equivalent to 0.1 pound of oil per pound of MLSS, the activated sludge system returned to normal within 24 hours (Ref. 123). The steel industry uses activated sludge treatment for wastewater containing phenols and cyanides (Ref. 32).

U.S. literature reports that selected microorganisms acclimated to phenol degradation (namely B. cereus) can metabolize concentrations of 1,000 mg/l phenol without exhibiting effects of toxicity (Ref. 20).

Russian literature reports that at Taishet and Orenburg railroad tie impregnation factories, wastewaters with phenol concentrations between 650 and 1,839 mg/l and brominable substances between 463 and 1,686 mg/l and tars and oils levels between 598 and 969 mg/l were treated by aeration tanks with activated sludge. Phenols were oxidized to up to 99.7% at both Taishet and Orenburg Plants, with effluent levels between 0.08-0.58 mg/l and 0.21-0.35 mg/l, respectively. Brominable substances were reduced by 90-93%, with residual concentrations of 25.4-69.9 mg/l at Taishet; and by 91.8% with residual concentrations of 51.3-91.7 mg/l at Orenburg. Tars and oils were reduced by 79.6-80.1% at Taishet and 64.8% at Orenburg; residues at Taishet being 13.3-16 mg/l and at Orenburg up to 212 mg/l (Ref. 52).

In terms of photoprocessing wastes, the activated sludge process rapidly biodegraded acetate, benzyl alcohol, hydroquinone, sulfite, and thiosulfate. Slow degradation occurred on developing agents, citric acid, ammonium salts, glycols, hydroxylamine sulfate, formalin, and formic acid. No degradation was evidenced for phosphate, bromide, ferrocyanide, borate, nitrate, and silver (Ref. 18). Activated sludge treatment is employed in the petrochemical industry for the bio-oxidation of hydrocarbons. Complete decomposition of 1.0 mg/l o-Benzyl-p-Chlorophenol mixed in sanitary sewage was achieved in one day of activated sludge treatment (Ref. 145). Bio-oxidation of propylene glycol wastewater from polyvinyl chloride production removed over 90% of the 1,000 ppm glycol component (Ref. 143). In another study of wastewaters from the production of polyhydric organics, acclimated mixed cultures removed about 90 percent of the influent propylene glycol and ethylene glycol (Ref. 144). Glycol, the main component of aircraft de-icing fluid, was reported present at 193 mg/l in a mixed sewage and de-icing fluid wastewater treated by activated sludge. The glycol was completely decomposed by the activated sludge process (Ref. 125). Another source reported the successful handling of the following organic wastes in various activated sludge systems: acetaldehyde, acetic acid, acetone, acrolein, high boiling alcohols, ethyl alcohol, formaldehyde, formic acid, glycerol, glycol, isobutyl alcohol, isopropyl alcohol, methanol, and phenolics (Ref. 38).

Application of activated sludge treatment in the pharmaceutical industry illustrates the ability of pure oxygen modes to handle large influent variations in organic content. The waste stream at Lederle Laboratories, Division of American Cyanamid, varies from about 900 to 10,000 mg/l COD and 300 to 3,000 mg/l BOD (Refs. 146, 95). High removal efficiencies are continuously maintained. The system was proven to handle shock loads when an accidental spill of 2,500 gallons methysolisol was received; within 8 hours the microbial population was respirating normally (Ref. 95). At one [illegible] part of the activated sludge system was employed to decompose a waste stream with [illegible]00 ppm BOD to an effluent of 100 ppm BOD. A detention time of 1-1/2 days was required, instead of the normal 8 hours (Ref. 95).

Activated sludge treatment systems are employed in at least two hazardous treatment facilities. At Hyon Waste Management Services, Inc., activated sludge treatment performs on a continuous basis (Ref. 96). At BioEcology Systems, Inc., activated sludge provides batch treatment (Ref. 116). Hyon claims treatment of wastes with up to 10,000 ppm COD*, BioEcology handles up to 30,000 ppm COD*. With an acclimated strain of microorganisms, a high enough MLVSS to minimize metals toxicity, a high dissolved oxygen content and long retention time, activated sludge processes can handle even higher waste loadings. It is suggested that processes using pressured air or pure oxygen can maintain necessary dissolved oxygen levels to handle waste streams of 300,000 ppm COD* (Ref. 117).

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*The assumed BOD:COD ratio is about 1:3 for these wastes.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

As can be seen, activated sludge treatment can be applied to a wide variety of aqueous waste streams as long as solids contents are low (generally less than 1%) and contaminants are predominantly organic. Activated sludge treatment should be seriously considered for any new waste treatment problems with wastes meeting these conditions.

C. EQUIPMENT AND MATERIALS

While the biochemistry of activated sludge treatment may be complex, the engineering design is very simple and relatively unsophisticated. The process involves open or closed tanks for the housing of aerobic microbes. Aerobic conditions are maintained in several ways: surface aerators may splash and stir the wastewater to incorporate air or pure oxygen, diffusors may bubble pressured air or pure oxygen into the wastewater. Pure oxygen systems require oxygen generating facilities.

The process relies on the continuous circulation of active portions of the biomass. Sludge recycle pumps return part of the biomass to the aeration tank from the secondary clarifiers.

Preliminary analysis of the wastewaters expected at the treatment plant determines the necessity for adding nutrients. If the influent is determined to be either nitrogen or phosphorus limited, the nutrient is added in determined amounts by a simple chemical feed system.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENVIRONMENTAL IMPACTS AND ENERGY REQUIREMENTS

The activated sludge system is basically environmentally sound, because it employs natural microbial metabolic processes for waste treatment. The activated sludge process is designed to encourage and enhance natural degradation. The primary energy demand is for maintenance of aerobic conditions in the system. The process is safe and reliable. The only significant emission is the biomass sludge. The sludge is a mixture of dead and living organisms, flocculated by their slimy cell coating, and containing nonbiodegradable inorganics and refractory organics by their adsorptive capacity.

B. ECONOMIC ANALYSIS

Wastewater flow rate, influent and effluent BOD levels, and average MLVSS are the critical design parameters for the activated sludge system. The system is energy intensive, meaning that over 10% of the total operating cost is based on energy needed for pumping, aeration and clarification. Reference 60 provided information for determination of electrical power consumption by the activated sludge system.

Capital costs reported in the literature for activated sludge processes are about 10¢/1,000 gallons for a 10-mgd facility. These costs increase to over $1/1,000 gallons for facilities handling less than 1 mgd. Activated sludge processes handling dilute wastewaters are reported to have total costs of 10-40¢/1,000 gallons.

We have developed costs for an activated sludge system as it might be employed in a hazardous waste treatment facility. The activated sludge process is necessarily preceded by clarification, neutralization and equalization so that a low solids content steady state waste loading may be received by the biological process. The costs are based on 1 mgd of wastewater with a BOD of 4,000 ppm. A relatively high food-to-mass ratio of 0.5 pounds BOD/day/1.0 pound MLVSS was employed so that metals inhibition would be minimized. An air-activated sludge system normally operates at an F:M ratio between 0.3 to 0.5, while a pure oxygen activated sludge system operates at an F:M ratio between 0.5 and 1.0 (Refs. 117, 118). As the F:M ratio increases, the necessary retention time for a fixed BOD applied influent decreases. The total unit cost of the system is shown as about $1.80 per 1,000 gallons of influent wastewater. See Figure 2 and Table 7.

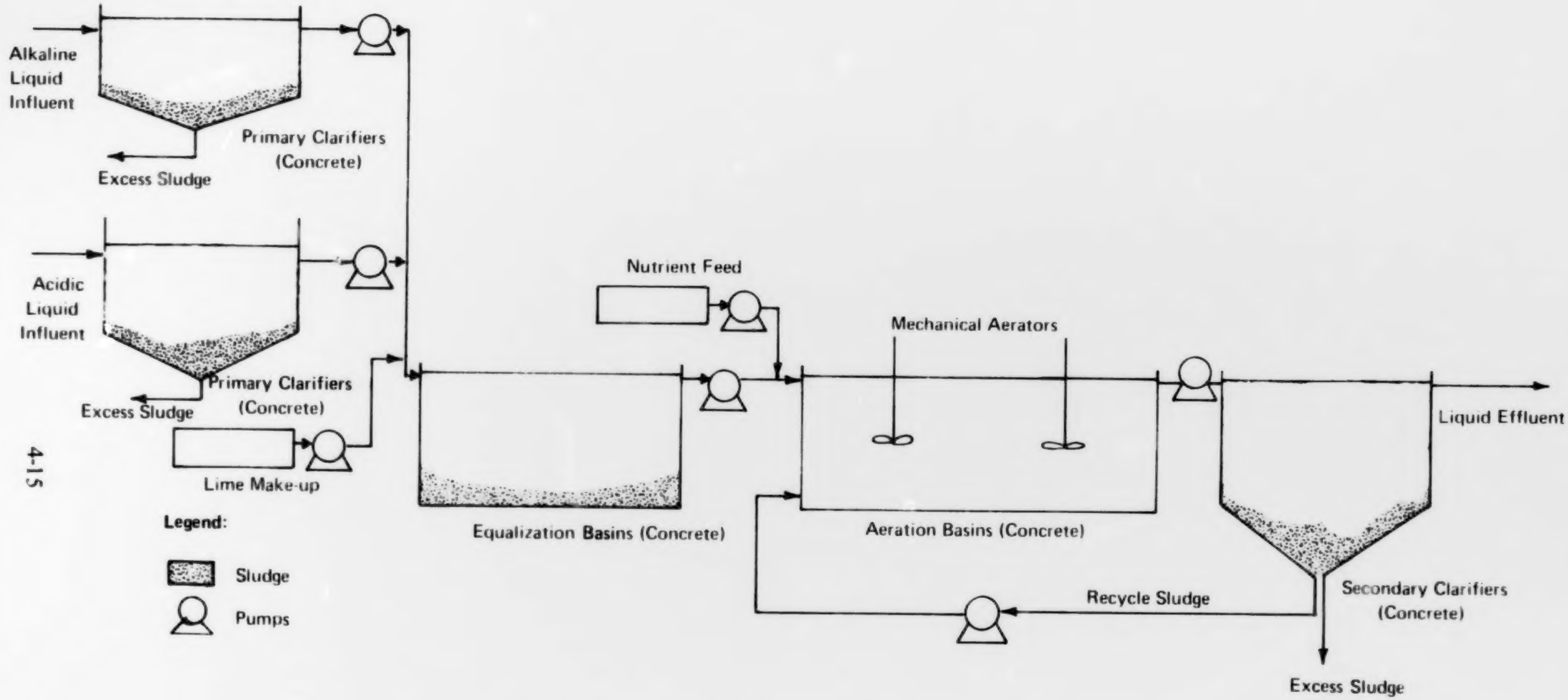

FIGURE 2 ACTIVATED SLUDGE TREATMENT COST BASIS FLOW DIAGRAM

TABLE 7

ESTIMATED UNIT COST OF ACTIVATED SLUDGE SYSTEM

Activated Sludge

Basis: 1×10^6 gallons/day, 10,000 ppm COD, 4,000 ppm BOD, 6,000 ppm MLVSS
365 day/year operation

Estimated Capital Investment: $1,900,000

	Annual Quantity	**Cost Per Unit Quantity**	**Annual Cost ($)**
Variable Costs			
Operating Labor	8,760 MH	$12.00/hr	$105,000
Maintenance (4% of Inv)			76,000
Lime	400 tons	$35.00/ton	14,000
Ammonia	330 tons	180.00/ton	60,000
Phosphoric Acid	180 tons	300.00/ton	54,000
Electricity	5.3×10^6 kWh	$0.02/kWh	105,000
Total Variable Costs			**$415,000**
Fixed Costs			
Taxes and Insurance (2% of Inv)			38,000
Capital Recovery (10 Years @ 10%)			311,000
Total Fixed Costs			**$349,000**
Total Costs			**$764,000**
Unit Cost ($/$10^3$ gal)			$2.09

Source: Arthur D. Little, Inc., estimates

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Activated sludge treatment is the optimum proven technology for biodegradation of organics in an aqueous waste stream. It is a relatively low cost system, employing no chemicals except for additive nutrients and employing energy primarily for the maintenance of aerobic conditions. Because of the high removals achievable for waste streams with organic constituents, it is already employed at two industrial waste treatment facilities. The process may be designed to receive effluent from other processes, or may receive raw waste which has been pH adjusted to neutral levels and equalized to steady-state organic levels.

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter VI of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

Anthony F. Gaudy, University of Oklahoma, Norman, Oklahoma.

Albert C. Petrasek, Jr., Texas A&M University, Dallas, Texas.

Jack McWhirter, Union Carbide, New York, N.Y.

Wesley W. Eckenfelder, Jr., Associated Water and Air Resources Engineers, Inc., Nashville, Tennessee.

Ross E. McKinney, Department of Civil Engineering, University of Kansas, Lawrence, Kansas.

BIOLOGICAL TREATMENT:

AERATED LAGOONS

Prepared by

Sandra L. Johnson

I. CONCLUSIONS AND RECOMMENDATIONS

Like activated sludge treatment, the aerated lagoon biological treatment process decomposes organics in aqueous wastewaters (less than 1% solids). The aerated lagoon essentially employs the same microbial reactions as the activated sludge. However, because the aerated lagoon does not have a sludge recycle system for continuous circulation of microorganisms, microbial strains do not acclimatize to the extent of activated sludge strains. BOD removal efficiencies for aerated lagoons range from 60-90%.

Costs for aerated lagoon treatment are slightly less than those for activated sludge treatment because of the lower construction materials investment for the lagoon basin. The cost for biomass sludge recycle is also eliminated in aerated lagoon treatment. Furthermore, aeration costs may be lower if full aeration is not a desired design feature. Total costs for dilute waste streams treated in earthen basins may range from 10-30¢ per 1,000 gallons, while total costs for more concentrated streams in lined basins may be nearly $2 per 1,000 gallons. Usually the aerated lagoons are designed to operate with minimal aeration and long retention times. Therefore, much larger land areas are required than for activated sludge systems.

II. PROCESS DESCRIPTION

A. BACKGROUND

The technique of aerated lagoons developed from adding artificial aeration to existing waste stabilization ponds. The aerated lagoon process employs mechanical or diffused aeration equipment similar to that found in the activated sludge treatment process. In fact, the process has been called a "dilute activated sludge" treatment process. The major difference with aerated lagoon treatment is that microorganisms are not continuously circulated from final clarifiers back to the head of the process.

B. UNDERLYING PRINCIPLES

Aerobic microorganisms (mostly bacteria) which are acclimated to the wastewater environment are used to decompose organic constituents in the influent aqueous media. The microbial system is essentially the same as the one described for the activated sludge treatment process. The microorganisms are able to decompose all types of simple and complex organics present in the influent waste stream.

As with the activated sludge process, aerobic lagoon treatment provides some trace metals removal. The aerated lagoon process may be slightly more sensitive to metal inhibition, because the biomass is not continuously circulated to encourage optimum acclimatization. Also, the aerated lagoon does not typically support the suspended solids levels achievable in activated sludge and able to minimize metals inhibition through adsorption. However, because of the longer retention times often evident in aerated lagoons compared to activated sludge, the micro-organisms provide less metals removal by adsorption.

C. OPERATING CHARACTERISTICS

The aerated lagoon process is similar to the activated sludge treatment process, except that there is no biomass sludge return. Because aerated lagoons are not generally as well mixed as activated sludge processes, a low level of suspended solids is maintained in the process mixed liquor. MLVSS of aerated lagoons generally range from 50 to 150 mg/l (Ref. 32). However, lower levels of mixing and aerating can be increased to levels comparable to activated sludge treatment so that higher MLVSS loadings can be supported.

The most important modification of the aerated lagoon process occurs when aeration is not sufficient to maintain aerobic conditions throughout the lagoon. A portion of the suspended solids, including biomass, is allowed to settle to the bottom of the basin and undergo anaerobic microbial decomposition. Lagoons having this characteristic are called aerobic-anaerobic or facultative lagoons. At the settled sludge/wastewater interface, facultative anaerobic bacteria decompose simple organics such as carbohydrates and proteins to volatile organic acids. These in turn are decomposed by obligate anaerobic bacteria which release methane as a product of anaerobic metabolism. See the report on anaerobic digestion for a more complete description of anaerobic microbial metabolic reactions.

The aerated lagoon system requires retention times which are slightly longer than activated sludge treatment. Retention times decrease as aeration facilities are improved to maintain dissolved oxygen levels comparable to activated sludge treatment. For facultative anaerobic lagoons, longer retention periods are necessary to support the slower metabolic rate of anaerobic microorganisms. Aerobic lagoons may require up to two days retention, while facultative anaerobic lagoons may need more than four days of retention time.

Aerated lagoons may be slightly more sensitive to surrounding temperatures than the activated sludge treatment process. In aerated lagoons, the best removal rates are achieved at temperatures about 30°C, with more than twice the retention time required at temperatures of 10°C (Ref. 11). For this reason, aerated lagoons are most often employed in temperate climates.

Longer retention times in the aerated lagoon process normally lead to endogenous respiratory conditions. This results in degradation of individual cell polysaccharide coating which is responsible for microbial flocculative abilities. High-rate activated sludge seldom involves endogenous respiration, and the biosolids are comparatively easy to flocculate and clarify. The longer retention times may allow biodegradation of refractory organics which break down more slowly.

D. EQUIPMENT AND MATERIALS

Usually, the aerated lagoon is a relatively deep (6-17 feet) earthen basin with mechanical aeration. The side walls of the basin are typically diked at a 3:1 slope. Clarification of the suspended solids in lagoon effluent is considered part of the total process.

For the treatment of industrial wastes, it may be necessary to line the basin. Recent linings for waste lagoons consist of pigment filled polyethylene or polypropyline. Hypalon. (DuPont) is excellent except for some solvents, ketones, chlorated solvents. The necessity for lining depends on the composition of the influent waste and the in-situ soil permeability.

III. APPLICATIONS TO DATE

The aerated lagoon biological treatment process has been successfully operated on petrochemical wastewaters (Ref. 26), textile wastes, pulp and paper mill wastes, cannery wastes, and refinery wastes (Ref. 38). The process is capable of decomposing all types of organics and can operate on the same categories of waste streams and organic species as the activated sludge treatment process.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements for aerated lagoon treatment are comparable to those for activated sludge treatment if the same design BOD influent and effluent loads are employed. Generally, the aerated lagoon employs less aeration and longer retention and results in lower BOD reduction efficiencies.

Chemical requirements are comparable to those for activated sludge treatment requirements, and essentially involve addition of nutrients.

B. ENVIRONMENTAL IMPACTS

Like the activated sludge treatment process, the aerated lagoon process results in a clarified liquid effluent and a biomass sludge residue. Because the aerated lagoons typically employ longer retention times resulting in endogenous respiration, the biosolids are more difficult to flocculate and settle from the mixed liquor.

C. ECONOMIC ANALYSIS

The principal equipment capital investment for aerated lagoons is for the aeration equipment. Another sizable portion of the capital investment is for earth moving construction costs. Where the soil conditions and influent waste composition require basin lining to prevent leachate, the capital investment increases markedly.

Operating costs are principally for aeration. The energy requirement for aeration may exceed 10% of the total waste treatment costs for aerobic lagoons. Nutrients are costly, and a nutrient-poor industrial waste would require substantial addition of nutrient chemicals.

Total costs reported in the literature for aerated lagoon treatment range from 10-30¢ per 1,000 gallons of dilute influent. For treatment of a more concentrated waste stream where a basin lining is required due to poor soil conditions, treatment costs may be nearly $2 per 1,000 gallons. Table 1 presents the total treatment costs for the aerobic lagoon system depicted in Figure 1. The costs are based on one million gallons per day of influent waste with 4,000 ppm BOD.

TABLE 1

COST ESTIMATES FOR AERATED LAGOONS

Basis: 1 x 10^6 GPD, 10,000 ppm COD, 4,000 ppm BOD, 90% Removal – 30,024 lb/day BOD, 365 day/yr operation

Estimated Capital Investment: $1,150,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor	8,760 MH	$12.00/hour	$105,000
Maintenance (4% of Inv.)			46,000
Lime	400 tons	$35.00/ton	14,000
Electricity	5.35 x 10^6 kWh	$0.02/kWh	105,000
Ammonia	330 tons	$180.00/ton	60,000
Phosphoric Acid	180 tons	$300.00/ton	54,000
Total Variable Costs			$374,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			$ 23,000
Capital Recovery (10% – 10 Years)			187,000
Total Fixed Costs			$210,000
Total Costs			$584,000
Unit Cost ($/$10^3$ Gal)			$1.60

Source: Arthur D. Little, Inc., estimates.

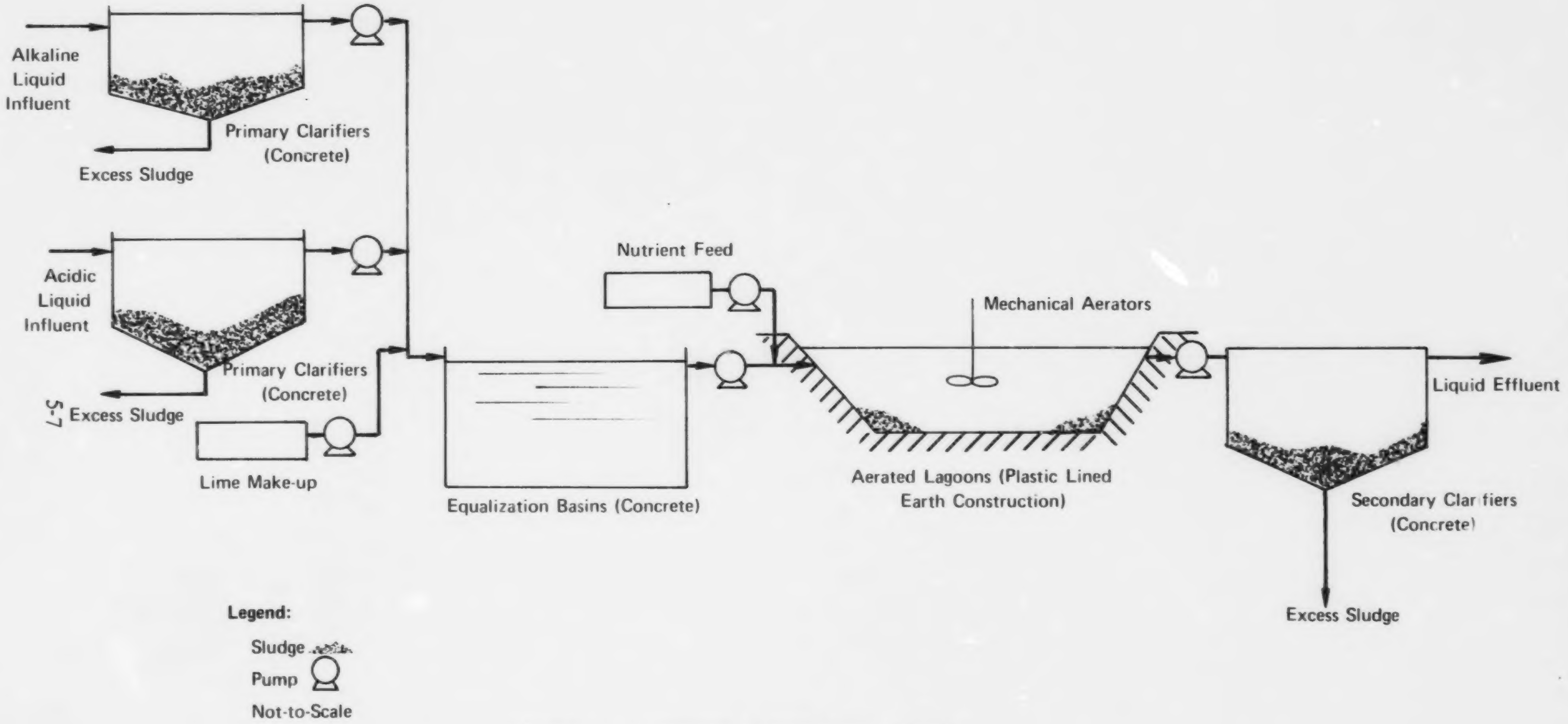

FIGURE 1 AERATED LAGOON TREATMENT COST BASIS FLOW DIAGRAM

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Compared to the activated sludge treatment process, the aerated lagoon biological treatment process is attractive for industrial waste treatment of organic wastes in temperate climates and where land area is not restricted. The removal efficiencies are not as high and the process is less flexible in maintaining effluent limitations under influent organic loading variations. Also, the aerated lagoon process does not have the advantage of continuous recycle of acclimated microorganisms. However, the longer retention periods often needed lead to further biodegradation of refractory organics and lower sludge production volumes.

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter VI of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

Wesley W. Eckenfelder, Jr., Associated Water and Air Resources Engineers, Inc., Nashville, TN.

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BIOLOGICAL TREATMENT: ANAEROBIC DIGESTION

Prepared by

Sandra L. Johnson

I. CONCLUSIONS AND RECOMMENDATIONS

Anaerobic digestion is a biological treatment process for the degradation of simple organics in an air-free environment. Anaerobic organisms utilize part of the carbon substrate for cell growth, and convert the other part to methane and carbon dioxide gas. Since anaerobic decomposition results in less efficient utilization of organic substrate for cell growth than aerobic decomposition the process has the advantage of low waste solids generation.

Anaerobic digestion is applicable only to simple organic waste streams—primarily carbohydrates, lipids, proteins, alcohols and organic acids (Ref. 27). Essentially no degradation of long-chain or cyclic hydrocarbons occurs (Refs. 89, 136, 150). The appearance of oil, fat and grease in the system is troublesome, causing scum formation and microbial inhibition (Ref. 32).

Metals concentrations are tolerated in the system as long as they are insoluble. Only soluble metal species are toxic to microbial activity, and generally the heavier the metal ion the greater the inhibition. At the neutral pH levels under which the anaerobic process must operate, most of the metals are precipitated as sulfides.

Economics on existing anaerobic digestion processes are not readily available because most digestors are municipally operated within a complete wastewater treatment facility. Our cost estimates indicate that digestion on a small scale, about 100,000 gallons per day, costs about $11 per 1,000 gallons, including amortization of capital investment. Overall, this process should be considered for treatment of industrial wastes.

II. PROCESS DESCRIPTION

A. BACKGROUND

Anaerobic digestion has traditionally been a supporting process in the field of biological treatment, in which the organic solids and biomass sludges from primary clarification and biological wastewater treatment are processed to reduce their volume and improve their stability. The process allows hydrolysis and fermentation to occur under anaerobic conditions, resulting in production of methane gas and reduction of the substrate carbon.

The anaerobic process is poorly understood because of its microbial complexity. Research is progressing to identify all of the types of microorganisms involved, including their symbiotic relationships and growth rate-limiting factors. Most of the research involves the use of sewage sludge as a growth substrate, because the process has been used mostly for sewage sludge digestion. Over the last 20 years, the process has been studied for meat packing wastes, cotton kiering liquor, brewery wastes, and alcohol distillery wastes (Ref. 89). As research progresses using other substrates, the anaerobic digestion process may gain greater acceptance as a first-order treatment process of industrial wastes.

B. UNDERLYING PRINCIPLES

The process depends on the symbiotic relation of two classes of microorganisms: acid-forming bacteria and methane-forming bacteria.

Acid-forming bacteria hydrolyze polysaccharides to monosaccharides and oxidize these to organic acids and alcohols, carbon dioxide and hydrogen (Ref. 74). The acid-forming bacteria are primarily obligate anaerobes, although some facultative anaerobes may be present in the mixed microbial population (Ref. 89). They perform oxidation by utilizing nitrites, nitrates, sulfates and organics as oxygen sources (Ref. 100). Therefore, the oxygenase enzyme catalysts in the microbes are accompanied by reductase coenzymes.

There is no evidence that complex hydrocarbons can be oxidized in the anaerobic digestion process. The anaerobic acid-forming bacteria do not appear to possess the enzymes capable of incorporating molecular oxygen into a hydrocarbon ring or chain.

Methane-forming bacteria utilize end products of the acid-forming bacteria's degradation of organics. All of the methane-forming bacteria are obligate anaerobes, capable of reducing acids and carbon dioxide to methane (Ref. 89). The methane-forming bacteria rely on the acid-formers for their substrate. It appears that they also rely on the acid-formers for their nutrients. For example, ammonia is produced from organic nitrogen compounds through the activity of acid-forming bacteria, and methane bacteria studied thus far require it as their main nitrogen source (Ref. 27). They appear unable to utilize the original nitrogen compounds, such as amino acids, for a nitrogen source.

The anaerobic digestion process results in low production of waste sludge. The volume of the influent sludge is substantially reduced, because organics are finally converted to gaseous end products of methane and carbon dioxide. Part of the microbial population incompletely hydrolyzes the substrate to alcohols and acids, resulting in little conversion of carbon to new cell growth. Another part of the microbial population converts the alcohols and acids to methane, which is rapidly discharged from the system because of its extremely low solubility in water. The continued removal of carbon from the system results in anaerobic cultures utilizing between 10-20% of the substrate carbon for cells. For comparison, an aerobic microbial population may use as much as 50% of the carbon substrate for conversion to cell mass (Ref. 89).

C. OPERATING CHARACTERISTICS

The anaerobic digestion system typically treats semi-solid organic wastes, averaging 5-7% solids content for ease of pumping and mixing (Refs. 27, 80, 81). A maximum of about 15% solids is tolerated by the system.

The conventional anaerobic digestor is a closed tank having no agitation mechanisms. Sludge is received in the middle zone of the tank where it is actively digested by the microbes. Methane and carbon dioxide are released from the microbial metabolic activity; these gases rise to the surface of the supernatant, lifting some sludge particles and some undigested greases, oils and fatty acids. As a result, a scum layer forms about the supernatant. The digested sludge is removed from the middle zone by gravity settling. Due to stratification in the digestor, digested sludge can be removed through the base of the tank and gas can be removed from the roof of the tank. Conventional digestors require a retention time between 30-60 days. The conventional process accepts up to 0.1 pound of volatile solids per cubic foot of digestion capacity per day. The influent sludge is reduced in volume by 40-60%.

High-rate anaerobic digestors are closed tanks with provisions for mixing. Mixing may be accomplished by mechanical agitators, gas circulation or pumping. There is no stratification of digested sludge, supernatant and scum as there is in conventional digestion. Frequently the high-rate digestor may appear in series with an unmixed digestor, so that settling of digested sludge and clarification of supernatant may occur. The high-rate anaerobic digestor requires a minimum retention period of 3 days, and averages 14-16 days. The process may accept up to 0.5 pound of volatile solids per cubic foot of digestion capacity per day.

The anaerobic contact process, a modification of the high rate digestion system, is used for waste streams of low solids concentrations. The process has received considerable attention by the meat packing industry, which produces a dilute waste stream compared to sewage sludge. The anaerobic contact process consists of a high-rate digestor followed by a settling chamber. Sludge is gravity settled and recycled back to the high rate digestor so that a high level of microorganisms is maintained within the digestor. Therefore, biomass retention is controlled independently of waste flow, and the slowly growing anaerobic bacteria are not rate limiting to the system. The hydraulic retention time for the anaerobic contact process is between 6-12 hours.

Other process modifications for anaerobic digestion are the anaerobic upflow contact process and the anaerobic upflow filter process. The anaerobic upflow contact process allows the slow upward movement of mixed liquor through a dense layer of microorganisms and substrate solids. The biomass layer entraps suspended solids until decomposition is accomplished. The biomass layer provides adsorptive capacity for soluble organics in the upward flowing mixed liquor. Upflow filter digestion is a laboratory-scale technique. The upflow filter consists of microbial accumulation on one or more filter beds of inert rock or plastic media. Research implies that longer microbial retention and shorter hydraulic retention periods may be achievable by this anaerobic digestion technique. The process would be primarily applicable to wastes with a low suspended solids content, otherwise clogging of the filter bed would result.

Anaerobic digestion is affected by factors of influent waste composition and concentration, pH and temperature. However, the overall rate is controlled by the rate of volatile acid conversion to methane and carbon dioxide (Refs. 27, 32). Therefore, the methane-forming bacteria are the rate-limiting microbes in the population. These bacteria grow slowly in digestors. Sometimes it takes 10 days for them to double in number (Ref. 84). Digestor upset occurs if the acid-forming bacteria are out of phase with the methane-forming bacteria, or when there is sufficient imbalance in their rates such that build-up of volatile acids occurs.

The methane-forming bacteria are highly sensitive to pH levels, operating best in a narrow range of pH of 6.8-7.5 (Ref. 89). Digestor pH levels may drop because volatile acids of CO_2 are produced in excessive quantities. This change may result from increased influent organic concentrations causing excessive acid-forming bacterial activity, increased hydraulic loading washing out the slow-growth methane-forming bacteria, and inhibitors slowing methane-forming bacterial activity (methane-formers are more sensitive to metal toxicants than are the acid-formers). Anaerobic digestion therefore requires steady-state operating conditions to maintain the microbial population in balance.

Alkalinity in the digestor buffers rapid changes in pH. High alkalinities are therefore desirable in a digestor. Alkalinity depends on the composition and concentration of influent wastes, as bicarbonates are formed from reduction of influent organics. High protein wastes provide higher alkalinities than high carbohydrate wastes (Ref. 27). pH of the digestor is buffered as acids not consumed by methane-forming bacteria react with bicarbonates to produce carbon dioxide. Decreasing bicarbonate and increasing carbon dioxide cause the pH level to fall. As a consequence, increased unionized volatile acid concentrations build up and result in inhibition of methane-forming bacterial activity. Hence, the concentration of volatile acids may continue to increase and gas production may decrease until the digestor fails. Little can be done to restore a failed system, except to empty the digestor and begin again. It may take several weeks to redevelop the digestor's microbial population.

Since the process of emptying a digestor is unpleasant, the anaerobic digestion process is generally closely monitored for volatile acids concentration and methane gas production. If acids build up, lime or bicarbonate may be added. However, municipal operators find it is best to stop the flow of influent waste, and allow the methane-forming bacteria to restore balance in the process (Refs. 80, 81).

Temperatures in the digestor are typically maintained between 31-35°C for conventional anaerobic digestion, and at about 37°C for high rate anaerobic digestion. Significant increases in gas production and volatile solids destruction accompany increases in temperatures, provided sufficient time is allowed for the microbial population to maintain the balance of acid-formers to methane-formers (Ref. 89). If temperatures in the anaerobic digestion process decrease, the methane production rate can be maintained by increasing the solids retention period so that more methane-formers are present in the system (Ref. 89).

The inhibitory effect of selected hydrocarbons on unacclimated anaerobic digestion was studied at Union Carbide (Ref. 83). Since the methane-forming bacteria are recognized as the most sensitive microorganisms in anaerobic digestion, inhibition was indicated by the rate of methane gas production. The study concluded that all of the aldehydes tested (formaldehyde, crotonaldehyde and acrolein) created inhibitory problems at 50 mg/l concentrations. Acrolein exhibited the most severe effects. Table 1 summarizes the results of the study. In general, inhibition was most pronounced in systems having high organic loadings (non-substrate limited). Decreased inhibition was evidenced as volatile acid concentration decreased. Acclimation of anaerobic digestion processes to the organic inhibitors studied was shown to be slow and relatively unsuccessful (Ref. 83).

D. EQUIPMENT AND MATERIALS

The anaerobic digestor relies on a closed reactor for the microbial population to function in an air-free environment. This reactor is typically built of concrete and has a floating cover which rests upon the upper surface of the sludge. The reactor may be partially buried in the ground, to minimize the effects of external temperature changes (Ref. 81).

Since methane-forming bacteria reproduce slowly, the population may be maintained by continuously circulating a portion of the sludge. The recycled sludge may also be passed through a heat exchanger so that temperatures are maintained.

Provisions for methane gas collection include a gas compressor on the top of the digestor. Gas is typically used to operate the heat exchanger. Remaining gas may be either wasted or utilized to run equipment in the plant. The gas produced from domestic sewage averages about 1 liter/gram of volate solids destroyed (Ref. 27). The gas is typically 30-35% carbon dioxide and 65-70% methane.

TABLE 1
IDENTIFIED PROBLEM CONCENTRATIONS OF TESTED MATERIALS[a]
(mg/l)

	Problem Concentration	
Chemical	**Substrate Limiting**	**Non-Substrate Limiting**
n-Butanol	–	>1000
sec-Butanol	–	>1000
t-Butanol	>1000	>1000
Allyl alcohol	–	>1000
2-Ethyl-l-hexanol	500-1000	–
Formaldehyde	–	50-100
Crotonaldehyde	~200	50-100
Acrolein	–	20-50
Acetone	–	>1000
Methyl isobutyl ketone	>1000	100-300
Isophorone	>1000	–
Diethylamine	–	300-1000
Ethylene diamine	–	100-300
Acrylonitrile	150-500	100
2-Methyl-5-ethylpyridine	>1000	100
N,N-dimethylaniline	>1000	–
Phenol	>1000	300-1000 (~400)
Ethyl benzene	>1000	–
Sodium benzoate	–	>300
Ethylene dichloride	150-500	–
Ethyl acrylate	600-1000	300-600
Sodium acrylate	–	>500
Dodecane	>1000	–
Dextrose	>1000	>1000
Ethyl acetate	>1000	–
Ethylene glycol	>1000	>900
Diethylene glycol	–	>1000
Tetralin	>1000	–
Kerosene	–	>500
Cobalt chloride	–	>1000

[a] Compound was arbitrarily classified as a problem when the activity ratio was less than 0.5. The 0.5 level was considered to be a decrease of more than 50% of the total gas production.

Source: Environmental Protection Agency, *Identification and Control of Petrochemical Pollutants Inhibitory to Anaerobic Processes,* 1973.

A chemical feed system may be needed for the addition of alkaline chemicals to buffer acid pH levels or for addition of sulfate compounds to precipitate soluble metals. Approximately 0.5 mg/l sulfide is needed to precipitate 1 mg/l of heavy metal (Ref. 27).

III. APPLICATIONS TO DATE

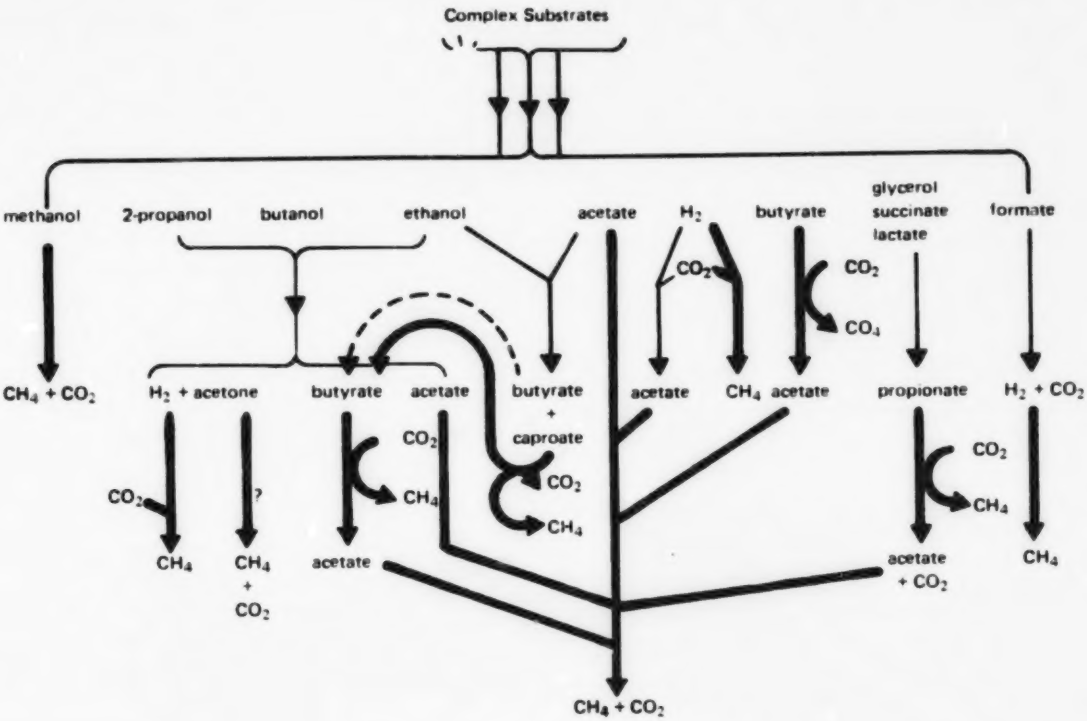
A. HISTORY

Scientists discussed their interest in the gases produced by decomposing animal and vegetative materials as early as 1682, and methane gas was first identified as "inflammable air" in 1776 (Ref. 27). In 1867 methane was produced from a single substrate, ethanol, and in 1887 methane was produced from fermentation of acetate as a substrate (Ref. 27). After the 1906 discovery that methane was produced from hydrogen and carbon dioxide, Barker and van Niel summized, in 1936, that methane fermentations were oxidation-reduction reactions in which energy yielding oxidations of numerous substrates may be balanced by the reduction of CO_2 to CH_4 (Refs. 27, 89). The fundamental kinetics of microbial growth were presented by Jacques Monod in 1949, and remain in general acceptance today for the design of anaerobic digestion systems under steady-state conditions (Ref. 89). In 1969, John F. Andrews developed a dynamic model (see Figure 1) for anaerobic digestion which considered un-ionized volatile acids as the growth limiting substrate and inhibiting agent of methane bacteria growth (Ref. 27).

B. CURRENT PRINCIPAL APPLICATIONS

The anaerobic digestion process has historically been used for the treatment of sludges from primary clarification and secondary biological treatment of municipal sewage. The process is used to reduce the volume of sludge, and to stabilize the organics for ultimate disposal. At the Deer Island Sewage Treatment Plant for Metropolitan Boston, the anaerobic digestion process destroys about 60% of the volatile solids, reducing the total solids content by about 40% (Ref. 80). The stabilized sludge is disposed of in the ocean, with no discernible adverse impact to the aquatic environment. Chicago's stabilized sludge is transported to abandoned strip mines purchased by the city, in which the sludge is used for land reclamation. The land reclamation project won the American Society of Civil Engineers' 1974 Award for an outstanding engineering achievement. In Philadelphia, digested sludge is made available to citizens for their yards. The digested sludge is called "Philorganic," and the give-away program is intended to limit the amount of digested sludge being disposed in the ocean.

In industry, anaerobic digestion has been employed in the meat packing industry. The first full-scale anaerobic digestion process for meat packing plant wastes was placed in operation in December, 1959, in Albert Lea, Minnesota (Ref. 92). Other meat packing industrial anaerobic digestors have since been built. The process generally includes preliminary equalization of flow, and preprocessing for removal of grease. The anaerobic digestion was shown to remove 90-96% of the BOD in a waste stream of 1,400 mg/l BOD at a digestor loading of 0.16 lb/day/cu ft (Ref. 92).



Source: *Anaerobic Biological Treatment Processes,* Advances in Chemistry Series 105, American Chemical Society, 1971.

FIGURE 1 INTERRELATIONSHIP BETWEEN THE METHANE BACTERIA AND OTHER SUBSTANCES OF THE ANAEROBIC CARBON CYCLE

Laboratory-scale digestion of cotton kiering liquor and alcohol distillery wastes were successfully achieved (Ref. 89). Laboratory- and pilot-scale studies on ground solid wastes mixed with sewage sludge showed that anaerobic digestion successfully reduced the waste volume, produced methane, and resulted in a stable end product similar to compost. The major difficulty encountered in the solid waste–sewage sludge digestion project was the formation of a heavy scum of flotable materials which could not be digested by the microbes. Researchers concluded that mixtures of refuse and sewage sludge with about 60% refuse could be digested. About 67% of the volatile solids were destroyed, and cellulose destruction was nearly 80%. No toxicity effects were observed (Ref. 91).

C. POTENTIAL APPLICATIONS TO INDUSTRIAL WASTE

Potential applications for the anaerobic digestion system include feed-lot wastes, culture material from pharmaceutical industries, and food-processing wastes.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy demands for anaerobic digestion are relatively low. Electrical energy may be required for mixing the reactor contents, recycling a portion of the effluent sludge to the reactor, and heating the incoming sludge. Essentially all of the power requirements for the heat exchanger should be met by the production of methane gas (Refs. 80, 81).

B. ENVIRONMENTAL IMPACTS

The anaerobic digestion system is not capable of significant decomposition of hydrocarbons with long chains or benzene rings. These organics are degraded by oxygenase enzymes present in aerobic microorganisms, but not in anaerobes. As a result, influent fats, greases and oils can result in scum formation in the digestor. The scum layer is especially troublesome in conventional anaerobic digestion, which does not involve continuous mixing of the sludge within the reactor. Eventual build-up of a large scum layer leads to closing down the process and manual removal of the scum (Ref. 81). Preprocessing of influent to the digestor may involve removal of oil, grease or flotables to levels less than 100 mg/l (Ref. 32).

Methane-forming bacteria in the system have been shown to catalyze transfer reactions. Transferase enzymes in the methane-forming bacteria may transfer active methyl groups in the organic substrate to acceptors such as arsenate and mercury (Ref. 27). As a consequence, the presence of arsenate or mercury in anaerobic digestors could lead to formation of toxic compounds.

C. ECONOMIC ANALYSIS

It is difficult to obtain existing economics for anaerobic digestion. In its dominant use in municipal wastewater treatment plants, its economies are not individually discernible. We have estimated the costs of anaerobic digestion for a small facility, daily treating 100,000 gallons of sludge with 5% solids. See Figure 2. The system design incorporates a preliminary equalization tank so that a steady-state composition and flow of sludge may flow to the digestor. The system also incorporates holding tanks to retain one day's digested sludge prior to ultimate disposal. It is assumed that there will be sufficient methane production to run the heat exchanger, but that additional power requirements must be paid. Table 2 presents our cost estimates.

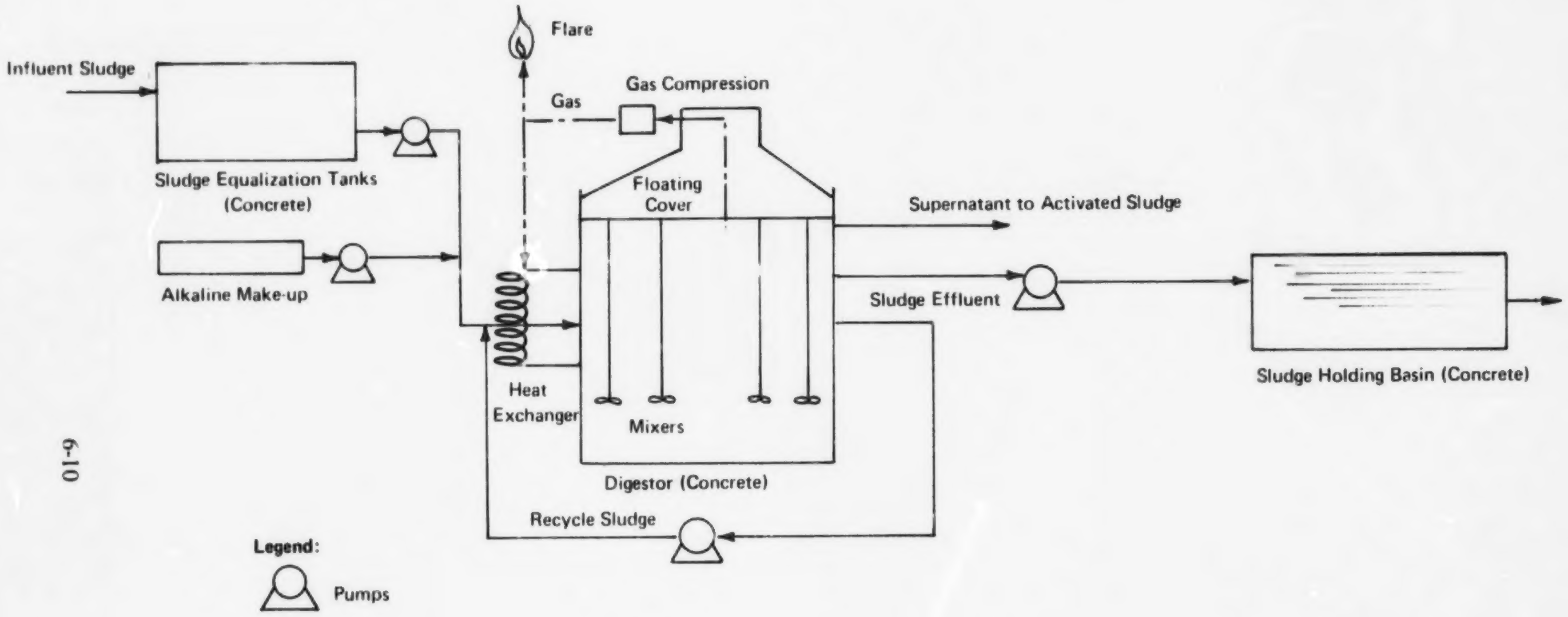


FIGURE 2 HIGH RATE ANAEROBIC DIGESTION COST BASIS FLOW DIAGRAM

TABLE 2

OPERATING COST ESTIMATES FOR ANAEROBIC DIGESTION SYSTEM

Basis: 100,000 GPD, 5% solids – 365 Days/yr; 0.5 lbs volatile solids per cubic foot of digestor capacity per day

Estimated Capital Investment: $1,250,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Cost			
Operating Labor	8,760 MH	$12.00/hour	$105,000
Maintenance (4% of Inv.)			50,000
Lime	200 tons	$35.00/ton	7,000
Electricity	450×10^3 kWh	$0.02/kWh	9,000
Total Variable Costs			$171,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			$ 25,000
Capital Recovery (10%–10 yrs)			194,000
Total Fixed Costs			$219,000
Total Costs			$390,000
Unit Cost ($/$10^3$ gal)			$10.69

Source: Arthur D. Little, Inc., estimates

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

The anaerobic digestion process offers distinct advantages for industrial waste processing. It reduces the volume of volatile solids, produces methane gas, and provides a stable, sludge residual amenable to land application.

The outlook for use of anaerobic digestion of industrial processing sludges is good if several constraints are incorporated into the system design. The process must receive a steady volume and concentration of influent waste having organics of low molecular weight; therefor, the system should be preceded by equalization basins. The process should not receive oil, grease and flotables; these can be removed by flotation prior to digestion. Soluble metals concentrations should be low; heavy metals may be kept insoluble by the addition of ferrous sulfate to encourage sulfides precipitation and light metal cations may be detoxified by encouraging formation of carbonates and bicarbonates.

With attention, anaerobic digestion can be operated continuously year-round. At the Deer Island sewage treatment plant, the digestors have operated wihout failure for more than six years. Prior failure was attributed to excessive sodium concentrations because of 25-30% seawater infiltration to the sewage collection system (Ref. 80).

Chicago's West-Southwest Treatment plant, reputedly the largest in the world—treating about one billion gallons of wastewater per day, has 12 digestors individually capable of handling 40 tons/day. According to operators at the Chicago plant, there has never been a failure requiring sludge removal from the digestor (Ref. 81). If volatile acids in a digestor increase above normal levels, the digestor is closed to influent until the microbial balance is reestablished. No addition of lime for pH control has been necessary, and no metals inhibition has been observed (Ref. 81).

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter VI of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

The following is a partial list of experts for anaerobic digestion:

John F. Andrews, Department of Environmental Systems Engineering, Clemson University, Clemson, S.C. 29631.

Perry L. McCarty, Department of Civil Engineering, Stanford University, Stanford, Calif. 94305.

Irwin Jay Kugelman, American-Standard, Inc., New Brunswick, N.J.

E.J. Kirsch, School of Civil Engineering, Purdue University, Lafayette, Indiana.

R.M. Sykes, Department of Civil Engineering, Union College, Schenectady, New York.

BIOLOGICAL TREATMENT:

COMPOSTING

Prepared by

Sandra L. Johnson

I. CONCLUSIONS AND RECOMMENDATIONS

Composting provides a means of achieving high-rate aerobic digestion of organics by mesophilic and thermophilic microorganisms. When waste is applied to the soil in windrow piles, and aerated by spreading or turning the pile, complete oxidation of simple and complex organics is achievable. In addition to microbial degradation, the process encourages adsorption of metals onto the soil-organic media.

It is the only biological treatment process which is relatively insensitive to toxicants. Between adsorption of solvent inorganics and precipitation of metals in the alkaline aerobic compost environment, inhibition is prevented.

Costs for the process are high, compared to other biological processes, ranging from 1¢-3¢ per gallon of waste. However, the costs are low when compared to incineration, which ranges from 15¢-20¢ per gallon of combustible waste.

Energy demand is very low, and is limited primarily to fuel costs to operate earth-moving equipment. Chemical requirements include limestone and nutrient addition.

There are no exotic compounds known to be formed. There are also no sludges or brines requiring ultimate disposal. Leachate from composting beds requires aqueous biological treatment, i.e., activated sludge treatment, for decomposition of solvent organics.

II. PROCESS DESCRIPTION

A. BACKGROUND

Composting has been practiced for centuries. Historically, composting involved leaving organic matter in piles or pits for decomposition prior to reuse. Composting became a systematic process in India and Italy in the 1920's, when the sequential piling and turning of vegetative matter and animal manures developed. In 1932, the first full-scale composting plant was established in The Netherlands, utilizing windrow piling for the decomposition of unground refuse. Between 1951 and 1969, eighteen composting plants were implemented in the U.S.; including the Johnson City, Tennessee, composting facility jointly sponsored by the U.S. Public Health Service and the Tennessee Valley Authority in 1966 (Ref. 30). Most of the U.S. composting plants have since closed due to lack of viable markets for the soil conditioning product. Composting has been more successful in Europe, the Middle East, and Asia where the need to add organic matter to the soil is more pronounced.

This report views composting as a disposal method, rather than a resource recovery method. In 1970, the process was implemented in Chicago for the disposal of high strength organic sludges (so-called hazardous wastes). While no humus product is recovered, the composting activity does provide a cost-effective disposal technique, costing over an order-of-magnitude less than incineration (Ref. 97).

There are over 30 composting process modifications identified by inventor or proprietary names (Ref. 30). This report considers windrow piling the fundamental process most commonly employed in the United States. It involves ground waste in open windrows, with a "haystack" cross-section, and aeration accomplished by turning windrows. Other process modifications employ rotating drums with forced aeration, silos with vertical decks with aeration accomplished as refuse is ploughed from deck to deck, structures with floors equipped to dump refuse onto the lower floor, etc.

B. UNDERLYING PRINCIPLES

Composting is essentially aerobic digestion of organics. It may take place within a structure, i.e., a silo or aerobic digestor, or it may be conducted on the land. Adequate mixing and aeration of waste is provided so that aerobic microorganisms perform decomposition or organics. When composting occurs on the land, the soil houses the microorganisms and performs an added function of adsorbing metals and refractory organics. Sequential mixing and turning of the soil mass is accomplished to maintain aerobic conditions. Because of the adsorption advantages of compositing on land, most of this report discussion will focus on that process modification.

The composting system relies primarily on long retention periods and acclimated aerobic microorganisms which perform hydrolysis and oxidation reactions to decompose organics. If the composting takes place in a soil media, fungi and facultative anaerobic microorganisms may also be present in the system. When the waste and soil piles are not turned adequately to maintain aerobic conditions, some anaerobic hydrolysis and oxidation of carbohydrates and proteins occurs. Microorganisms necessary for composting activity are present in the original substrate. In windrow piling,they are present in the soil as well as the organic substrate. Addition of microorganisms from foreign sources has proved to be of little value (Ref. 30).

When composting begins, the microorganisms are predominantly mesophilic. As temperatures increase to more than 40°C, thermophilic microbial species predominate.

In systems employing soil media for composting, metals inhibition of microorganisms has not been apparent. At the Hyon Waste Management Services, Inc., facility which employs composting of hazardous wastes, metals have not inhibited microbial activity. The pH levels are kept neutral to alkaline, and the compost beds are sequentially spread and piled to maximize aerobic conditions. As a result, metals are present as oxide, hydroxide, and carbonate precipitates, if they are not adsorbed or exchanged onto the soil or organic media (Ref. 98). In land farming of oils, lead concentrations between 7,000 and 15,000 ppm were shown to have no effect on the soil's microbial flora (Ref. 99). Similar studies on vanadium concentrations in oils showed no effect on microbial flora (Ref. 98).

The mixed microbial system is able to destroy nearly all types of organic compounds. Oils are commonly applied to the soil in land farming of petroleum refinery wastes, and are susceptible to being oxidized by soil microorganisms within several years (Ref. 96). The primary mechanism for microbial decomposition is enzyme catalysis of oxidation, with exoenzyme oxygenases secreted from the cells. Within one year, oil concentrations in soils were proved reduced by 50-90% of their original levels (Ref. 106). Raymond, *et al.* has demonstrated the oxidation of paraffinic, cycloparaffinic and aromatic hydrocarbons by soil microorganisms, so long as more simple organics were present as substrate for cell growth (Ref. 104). Intermediate byproducts of the microbial oxidation included organic acids, alcohols, aldehydes, and ketones. Some of the aromatics may polymerize to form resins which then take longer to biodegrade.

To date, halogenated aromatic hydrocarbons have been found the most resistant organics to significant degradation by typical microbial populations (Ref. 97). At the Hyon facility, only the halogenated hydrocarbons (i.e., polychlorinated biphenyl) are not applied to the compost beds and are, instead, incinerated (Ref. 97). On the other hand, a microbial population may be developed and acclimated to handle even these most refractory organics. Although pentachlorophenol is cited as one of the most refractory organic compounds, an aerobic bacterium has been shown to metabolize pentachlorophenol as a sole source of organic carbon and energy (Refs. 101, 102).

C. OPERATING CHARACTERISTICS

Applied loading rates for composting are not readily established. Acceptable loading depends on the biodegradability of the organic constituents, the microbial acclimitization to influent waste, substrate, nutrient availability and climate.

In land farming of refinery activated sludge. Exxon applies 70 tons of dewatered (about 15% solids) sludge per acre per month and believes 100 tons monthly would be assimilated by the land (Ref. 97). The applied loading was equivalent to about 0.4 gal/sq ft per month dosing rate with 15% solids.

Land farming oily sludges, containing 33% oil, in an EPA demonstration project involved applying 70 barrels per acre per month (Ref. 107). This was equivalent to about 0.07 gal/sq ft per month. Land farming of oils added in a single application for investigative purposes by Sun Oil involved a loading of 11.9 $m^3/4 \times 10^3$ m^2 (Ref. 106). This was equivalent to about 0.07 gal/sq ft.

At Hyon, loadings of 10 gal/sq ft per month of aqueous waste streams averaging 3-5% solids are applied to the compost beds (Ref. 97).

Moisture content is an important criterion for compost optimization. Excess moisture restricts aeration, while limited moisture deactivates microbial enzymes. Studies on municipal refuse have established moisture contents between 63-79% as optimum. Higher moisture contents are permissible for porous mixtures of straw and manure (Ref. 110). Addition of pulverized limestone further increases acceptable moisture levels (Ref. 98).

Temperature is the fundamental parameter for measuring composting activity. At the beginning of composting, temperature in the waste is the same as ambient air temperatures. As the organisms dissimilate organics, and synthesize new cells, heat is released and temperatures in the compost pile rise. At about 40°C, mesophilic microorganisms die off, to be replaced by thermophilic microorganisms. As temperatures increase to as high as 70°C, microbial activity accomplishes rapid decomposition of organics. Once the waste substrate is fully decomposed, temperatures in the pile return to ambient levels (Ref. 114). The sequence of speading-dosing the compost bed, then farming the windrow piles should be scheduled to optimize thermophilic microbial activity.

Alkaline aerobic conditions are maintained in composting so that metals are not soluble, and therefore, potentially toxic to microorganisms. Nutrients are added, as needed, to supplement the carbon-nitrogen-phosphorus ratio of incoming wastes. Wood chips, manure, etc., are provided to maintain a simple organic substrate for cell growth.

The windrow pile composting process operates continuously year-round. Total retention times necessary for organic wastes to be degraded average three to four months. Within one year, even refractory organics should be oxidized. An optimum composting procedure, as established at Hyon, would follow the following steps:

- 3-4 Weeks – Spread the media and organisms into flat beds of about 2 inch thickness.

  – Dose with waste, lace with nutrients (nitrate) and alkalines (lime and calcium carbonate).

- 7-10 Days – Pile media, organism and waste mass into compost windrow forms about 4 inches high.

- Repeat flattening of beds for aeration.

- Repeat waste dosing, nutrient addition, pH adjustment.

- Repeat windrow piling.

Location of windrow piles is alternated so that each biochemical bed's bottom does not get mucky and impervious. An aerated pervious bed bottom allows continuous leachate drainage.

D. EQUIPMENT AND MATERIALS

The only equipment essential to windrow composting is an earth-moving machine for turning and piling waste. For composting of industrial processing sludges, we assume that open tanks, pumps and chemical feed systems are needed to provide neutralization and equalization of influent prior to application to the compost beds.

Provisions for collecting leachate and runoff waters from the compost beds are necessary to protect groundwater from solute transport of solvent organics, and metals. Either a concrete slab with sump drainage or a pattern of underground perforated pipe could be employed to collect leachate. Surface ditches could collect runoff water.

III. APPLICATIONS TO DATE

Composting has primarily been applied to combinations of municipal refuse (both ground and unground), animal manure, vegetative matter and sewage sludge (Ref. 30). Noncombustibles such as plastic, glass and metal are removed prior to composting.

Composting has been practiced for cannery solids, pharmaceutical sludge and meat packing wastes. Windrow piles used to compost pharmaceutical wastes have accomplished full decomposition within 25-28 days, achieving internal windrow temperatures between 50-60°C. At Lederle Labs Division of American Cyanamid, compost product from decomposition of pharmaceutical sludges is provided to community gardeners (Ref. 95).

Primary sludge from Chicago's municipal waste treatment is composted by allowing long retention on large drying beds. The stabilized sewage sludge, so-called "Nu-Earth," is officially offered for lawn use to citizens by the Board of Trustees of the Metropolitan Sanitary District of Greater Chicago.

Petroleum refineries often dispose of oily wastes by land farming, a compost process of spreading and tilling oily wastes into soil. A typical 100,000 barrel per day refinery might generate 5,000 to 100,000 barrels per year of oily wastes requiring disposal (Ref. 154). Generally, full decomposition of oils is achievable within three years of application.

IV. ECONOMICS, ENVIRONMENTAL ISSUES AND ENERGY

A. ENERGY REQUIREMENTS

Energy demands are minor, primarily attributed to pumping and heavy equipment fuel costs.

B. ENVIRONMENTAL IMPACTS

The only emissions from composting are carbon dioxide, steam, a liquid effluent containing partially oxidized organics in solution, and a barn yard smell. The musty barn yard odor is indicative of healthy microbial activity. Septic odors result only when the bed is not adequately turned to maintain aerobic conditions. When a windrow pile stops steaming, it is apparent that internal temperatures have returned to ambient levels and the organic substrate is either fully composted or has leached from the bed.

There need be no sludge disposal attributed to composting. All organic substrate remaining on the compost bed is fully oxidized. This is generally evidenced by shrinkage of the compost bed, unless new wastes are continuously added. At Hyon, no disposal of bed solids has ever been necessary, nor is it envisioned (Ref. 97).

C. ECONOMIC ANALYSIS

The costs for composting of industrial processing sludges are based on using the windrow pile process, because of the benefits of employing soil in the process for metals and refractory organics adsorption. The costs also provide for addition of wood chips to the windrow pile, so that a continuous biodegradable organic substrate is available to supplement the variable influent waste composition. Also, the wood chips aid in the adsorption of metals and refractory organics. The adsorption of metals renders them non-inhibitory to the microbial population, as only solvent metals are toxicants. The adsorption of refractory organics renders them immobile until microbial decomposition is performed.

Pulverized lime is added to the windrow piles to maintain pervious aerated piles and neutral pH levels. Nutrients are added to enhance the rate of decomposition. Data on land farming of oil indicate a direct relationship between the quantity of fertilizer added and the oil removal rate, with removal increasing proportion to nutrient addition (Ref. 107).

Figure 1 shows a schematic of the composting system upon which costs in Table 1 are based. The influent waste stream is neutralized and equalized before application to the compost bed. The waste can be either hosed, spread or sprayed onto the beds. As seen in Figure 1, we have based costs on a spray dosing system as solids levels averaging in excess of 5% are not expected. Although Hyon designed its compost system for receipt of 30% solids waste streams, they are averaging 5% solids in receipts (Ref. 98). If more concentrated solids loadings are received at the model facility, the on-site heavy equipment could be used to shovel or spread the waste onto the pile.

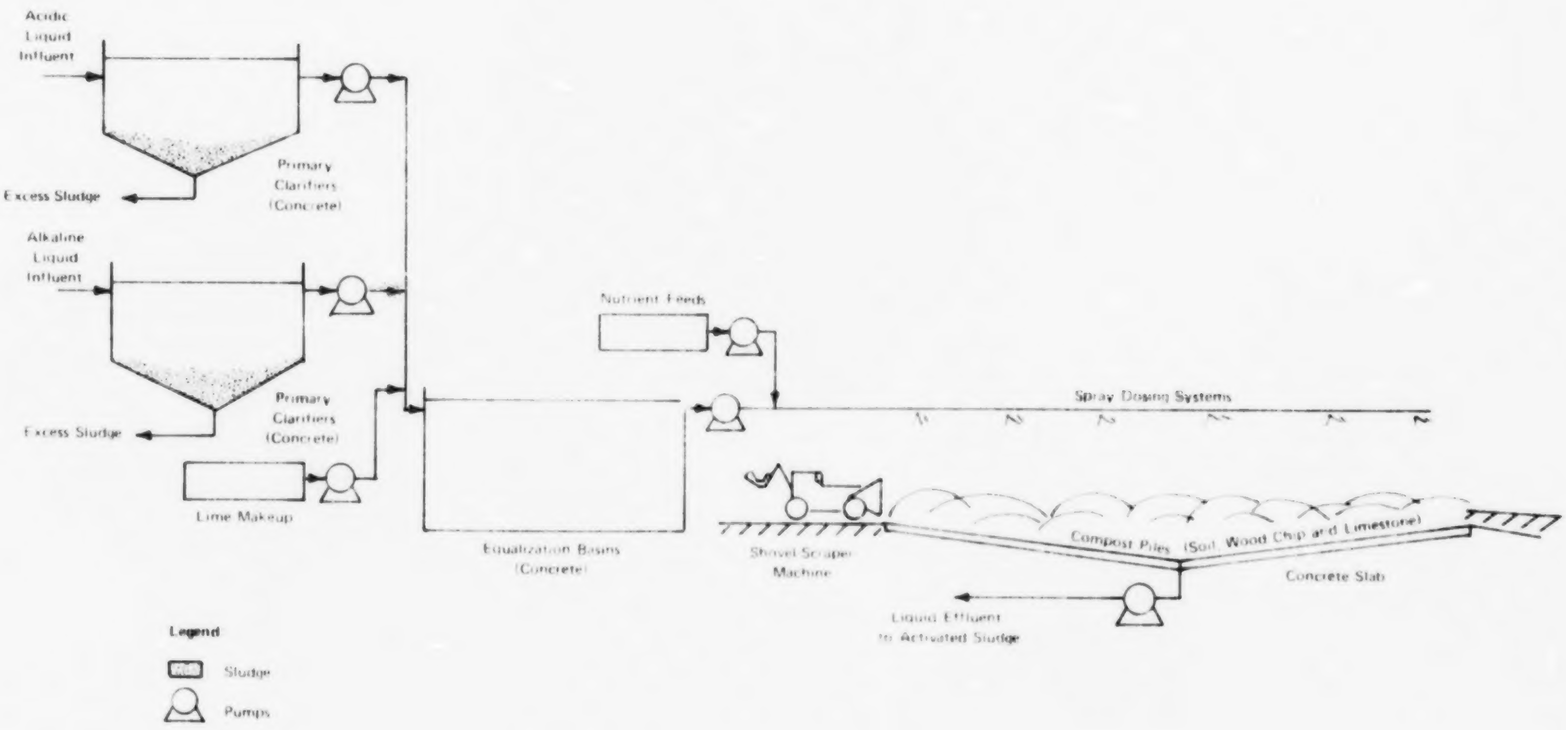


FIGURE 1 BIOCHEMICAL BED-COMPOST SYSTEM COST BASIS FLOW DIAGRAM

TABLE 1

ESTIMATED OPERATING COSTS FOR COMPOSTING SYSTEM

Basis: 100,000 Gallons/Day; COP-200,000 ppm, BOD-50,000 ppm, 365 day/yr operation
Estimated Capital Investment: $1.5 x 10^6

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Cost			
Operating Labor	8,760 Hours	$12.00/Hour	$ 105,000
Maintenance (2% of Inv/Year)			28,000
Electricity	75,000 kWh	$ 0.02/kWh	1,500
Limestone	8,000 tons	$10/ton	80,000
Wood Chips	6,000 tons	$10/ton	60,000
Fuel Oil	30,000 gal	$0.60/gal	18,000
Ammonia	1,500 tons	$180.00/ton	270,000
Phosphoric Acid	800 tons	$300.00/ton	240,000
Total Variable Costs			$ 802,500
Fixed Costs			
Taxes and Insurance (2% of Inv.)			$ 30,000
Capital Recovery (10% – 10 Yrs)			245,000
Total Fixed Costs			$ 275,000
Total Annual Costs			$1,077,500
Unit Costs ($/$10^3$ gal)			$29.55

Source: Arthur D. Little, Inc., estimates.

Costs for the diagrammed compost system are nearly $30/1,000 gallons of influent waste. These costs do not include treatment of the collected leachate from the compost beds. Approximately $5/1,000 gallons might be added to composting costs, for activated sludge treatment of leachate followed by polishing of effluent in waste stabilization ponds.

Capital costs shown on Table 1do not include land acquisition expenditures. The major portion of the operating costs are attributed to chemical additives for nutrients and pH control.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Composting provides a viable means for decomposing all types of organics by microbial activity. The process relies on aerobic microorganisms which periodically achieve very high oxidation rates at thermophilic temperatures (above 40°C).

There is no measurable inhibition of microbial activity attributed to metals concentrations. The soil and organic media provide adsorption for metal ions, and alkaline aerobic process conditions are maintained to keep metals insolvent.

There is no sludge residue requiring ultimate disposal. Organics, including dead microorganisms, are ultimately decomposed to carbon dioxide and water, as well as some solvent organics which leach from the compost beds. Hyon estimates that applying an aqueous waste stream of 200,000 ppm COD to a compost bed may result in 10,000 ppm COD in the leachate (Ref. 97). On the other hand, Raymond (Ref. 99) has found no evidence of partially oxidized hydrocarbons leaching from oil land farming operations, and postulates that the mixed microbial population allows some organisms to utilize the partially oxidized end products developed by other organisms.

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter IV of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

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BIOLOGICAL TREATMENT: ENZYMES

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

Enzymes are simple or combined proteins acting as specific catalysts. The most characteristic property of enzymes is the striking specificity which manifests itself in their catalytic action. A given enzyme catalyzes only the reaction of an individual group of compounds, a single type of compound, or even a certain kind of bond in a given compound. For enzyme treatment of wastes to proceed, the enzymes must first be separated from living cells, segregated into reliably pure and active forms, maintained within the appropriate environment, "immobilized" by attaching them to solid media to avoid their being washed away, and coupled with the specific phase of the chemical reaction they each address and the appropriate co-factors (i.e., energy sources) necessary for their function.

Attempts to add enzymes to activated sludge biological treatment systems handling mixed wastes have been unsuccessful. The multitude of enzymes already present in the microbial environment provided a hostile environment for enzymes not normally associated with the specific organisms involved. Also, it was found that the rate limiting enzymes were found within the cell walls (endoenzymes), and the speed of decomposition was not improved by adding enzymes outside the cell wall (exoenzymes) (Ref. 65). There have also been studies on addition of enzymes to sludge digestion systems, and the results have showed no significant improvement.

It is doubtful that use of enzyme treatment at a facility receiving varying hazardous waste mixtures would be economically feasible. Enzymes cannot adapt or acclimate to varying substrates. Also, they are inhibited by presence of soluble inorganics and highly sensitive to pH and temperature levels. It is doubtful the enzyme treatment could compare economically with biological treatment, even on relatively pure waste streams, unless resource recovery were the principal objective.

II. PROCESS DESCRIPTION

A. BACKGROUND

In 1926, the first enzyme was isolated in crystalline form. In the 1950's the work of Nikolaus Grubhofer and Lotte Schleith of the Institute for Virus Research in Heidelberg, West Germany, popularized the concept of immobilizing enzymes by reportedly covalently binding them to diazotized polyaminostyrene (Ref. 64). Since then a number of immobilization techniques have been developed. Once immobilized, the expensive enzymes were able to be reused and research on enzymes was stimulated. In 1960, the complete configuration of amino acids in ribonuclease was determined. Determination of more complex enzyme structures soon followed as X-ray technology was used. Beginning in about 1968, ribonuclease was synthetically constructed by joining together its 124 amino acid chain. In 1971, in the United States, the National Science Foundation formed an enzyme technology program in its Research Applied to National Needs (RANN). Initially, the NSF program provided 11 research grants totalling $531,000. Peak financing occurred in 1973, when $2.3 million of research grants were awarded. The 1975 program provided 21 projects with a cumulative total of $1.5 million. In addition, there are numerous biological and medical NSF and NIH grants outside the enzyme program which provide knowledge inputs to the field of enzyme technology (Ref. 64).

B. UNDERLYING PRINCIPLES

Enzymes are chemical catalysts derived from organisms. Nearly all biochemical reactions are catalyzed by enzymes which are specific to the substrate being acted upon. There are nearly 2,000 known enzymes. No single species or cell has all of them. Species which predominate in a given environment are those with the necessary enzymes to catalyze biochemical reactions vital for cell growth.

Enzymes act as catalysts by lowering the activation energy needed for chemical reaction to occur. They are usually not permanently changed by the reaction process. Electron manipulation is a requirement for the catalytic activity. The enzyme becomes a part of the chemical reaction; but after the reaction is complete, the enzymc is usually split off, unchanged and ready to catalyze another reaction.

Enzymes are generally selective and act upon specific molecules. Enzymes may be thought of as a three-dimensional structure with grooved active sites, and only selective molecules can fit the grooves (Ref. 66). When the enzyme and substrate molecule collide at the active site, the chemical reaction is catalyzed and decomposition products released.

There are levels of enzyme specificity, according to Ref. 66. There are "absolute" enzymes which catalyze reaction of only one substrate. Urease is an absolute enzyme and works only to break down urea into carbon dioxide and ammonia. "Stereospecific" enzymes react only with one type of optical isomer, and catalyze reactions of related compounds of the same configuration. "Hydrolyzing" enzymes react with a specific type of chemical linkage, irrespective of the radical groups. Still other enzymes function by breaking the chemical link only if the groups fit the active enzyme site; these may work by removing one group after another from a chain molecule and would be unable to attack the chain center.

The International Union of Biochemistry has characterized enzymes into six major groups according to their function:

Enzyme	**Function**
Hydrolases	cleave molecular bonds by hydrolysis
oxidoreductases	catalyze oxidation or reduction reactions
transferases	transfer radicals other than oxygen or hydrogen, e.g., phosphate
isomerases	isomerize molecules, change their atomic arrangement
ligases	join molecules, e.g., synthesize protein, carbohydrate and nucleic acids
lyases	cleave bonds by removal of radical groups

Most of the enzymes fall into the first two categories of hydrolases and oxidoreductases. These are also the two categories most applicable to decomposition of waste. The individual terms for each enyzme are formed by linking the prefix of the substrate name with the suffix "ase." For example, the enzyme which acts on urea is called urease, and the enzymes which act on protein substrates are called proteases.

Enzyme reactions on polysaccharides (carbohydrates), polypeptides (proteins), fats, nucleic acids involve degrading polymers to their monomeric units by hydrolysis. This involves the incorporation of water into the molecules as the polymer is broken down. After the hydrolysis products (e.g., sugars, glycerol, fatty acid, and amino acid) from polysaccharides, fats and proteins are developed, they may then be converted to lower molecular weight fatty acids or alcohols (e.g., lactic and acetic acid) and further still to methane, carbon dioxide and water by oxidation and reduction reactions (Ref. 75).

All complex hydrocarbon organics are subject to degradation by oxidation. Oxygenases may oxidize the terminal methyl group of straight chain hydrocarbons to alcohols and acids by incorporating oxygen directly into the molecule. Oxygenases usually catalyze introduction of both oxygen atoms of the bimolecular O_2 as follows:

$$RH_2 + O_2 \overset{\text{oxygenase}}{\qquad} R\,(OH)_2$$

According to Ref. 75, there are three types of oxygenase. Oxygenase type-one cleaves aromatic rings such as the benzene, phenol, and catechol. Oxygenase type-two works on nonaromatic rings by cleaving the ring, but allowing ring reformation with one less carbon atom. Oxygenase type-three oxidizes lipids. Another group of oxygenases are called hydroxylases, which incorporate a single atom of the bimolecular O_2 into the matrix.

Enzymes, because they are very selective regarding molecules that fit their active sites, do not perform as readily on branched hydrocarbons as straight-chain hydrocarbons. Also, unsaturated hydrocarbons are more amenable to enzymatic catalysis than saturates. Hydrocarbons are made recalcitrant to degradation by substituting halogens on the molecules. Also, polymerization of hydrocarbon molecules increases resistance to enzyme catalysis. Lignin is a polycyclic aromatic which is resistant to degradation. To decompose chlorinated hydrocarbon pesticides, enzymatic activity would involve hydrolases, oxidoreductases, transferases, isomerases and lyases (Ref. 75).

There are two classes of enzymes, exoenzymes and endoenzymes. Exoenzymes are produced within the cell but are secreted outside the cell to hydrolyze complex organics to a size that can pass through the cell water. The endoenzymes are active inside the cell wall to convert the partially hydrolyzed organic to products for cell growth and reproduction (Ref. 78). In enzyme production, it is easiest to obtain exoenzymes. Endoenzymes are difficult to obtain because it is difficult to separate the enzyme proteins from other cell proteins (Ref. 35). The exoenzymes may be more desirable than the endoenzymes, because they catalyze reactions on the more complex substrates. The hydrolases which catalyze hydrolysis reactions, are primarily exocellular.

Animals, plants, and microorganisms can serve as enzyme sources. The microorganisms provide the optimum source for waste treatment because the appropriate enzymes are present in bacteria and fungi which naturally perform biological decomposition of organics. The microorganisms are also free of seasonal limitations. Genetic engineering with microorganisms is a developing science to produce greater yield of enzymes and new enzyme capabilities. The genetic methods could lead to production microbially of new synthetic enzymes with desirable catalytic properties. Eventually it may be commercially feasible to produce synthetic enzymes without using living organisms (synthesis of ribonuclease of 12,700 molecular weight has been accomplished by Merck & Company at Rockefeller University (Ref. 67).

C. OPERATING CHARACTERISTICS

The rate of reaction catalyzed by an enzyme is usually much faster than by a nonbiological catalyst. A single enzyme can convert up to 10^7 substrate molecules to product in a second (Ref. 65). One molecule of catalase enzyme can convert 10^6 molecules of hydrogen peroxide per second. Their activity is attributed solely to the pattern of amino acids, and particularly to the configuration of exposed reactive groups. A large enzyme molecule may have a number of reactive sites on its surface (Ref. 66). Enzymes are long chains of amino acids, with molecular weights known to range up to 1 million.

Enzyme catalysis is a function of the enzymes' colloidal and protein character. The enzymes are affected by heat, and may lose catalytic effects at high temperatures. They are also sensitive to pH; and function at an optimum pH which depends upon the buffer system present, the presence of other colloids, and adsorbed ions. Enzymes, which are able to combine with other compounds by adsorption, may adsorb inorganic ions, particularly metals. A chemical reaction may result in the introduction of a complex which enhances enzymatic activity. There are, however, some metals, mainly heavy metals, which impede the catalytic action of enzymes (Ref. 29).

Many proteins appear to be stable in dilute solution at low temperatures, but show increasing instability as water is removed. Enzymes are known to be intolerant to temperature changes of more than a few degrees from their optimum. Each enzyme has a unique optimum temperature. Researchers are investigating microorganisms which grow to high temperatures (40°C and above) in order to isolate enzymes with increased heat stability (Ref. 64). Other researchers found that excluding oxygen and adding a reducing agent enhanced the stability of their enzyme preparations under greater temperature ranges (Ref. 64).

Extensive enzyme purification may both decrease enzyme stability and increase process cost (Ref. 64). Impurities often offer some protection against deactivation. Many industrial enzymes are sold in an impure state to achieve a reasonable shelf life (Ref. 66). On the other hand, proteases, which are enzymes which persist through many purification processes, decompose other enzymes. Addition of chemical protease inhibitors helps alleviate the protease problem (Ref. 64). Although researchers often separate each enzyme into pure states for study of individual catalytic reactions, this would probably not be required for enzyme degradation of a waste component through several reaction steps. Proponents of enzyme treatment note that use of whole microorganisms may contain a thousand unnecessary, and perhaps inhibitory, enzymes to perform a sequence of chemical reactions. As techniques for enzyme isolation and immobilization improve, it may eventually become worthwhile to utilize enzymes rather than whole cells for treatment of a relatively pure waste stream. Use of purified enzymes specific to a waste component implies that no extraneous exocellular enzymes would be added to the final effluent. Also, use of enzymes results in no cellular sludge.

The activity of an enzyme is highly influenced by the substrate pH, implying that the ionic condition of reactive groups is a major factor in enzyme catalysis. The pH determines the electron density in the active sites of the enzyme. This affects whether the active sites attract electrons from substrate molecules or protons. The optimum pH for enzyme-substrate reactions varies widely. This is evidenced by the differences in optimum pH for microorganisms such as acid-forming bacteria versus methane-forming bacteria found in the anaerobic digestion process; both types of bacteria contain separate sets of enzymes with acid-forming bacteria functioning best under acidic conditions and methane-forming bacteria functioning only under neutral conditions. Table 1 shows the wide differences in optima pH for several enzymes. At extremes of pH from the optimum range, inactivation of the enzyme occurs rapidly and is irreversible.

TABLE 1

DIFFERENCES IN OPTIMA pH FOR SEVERAL ENZYMES

	pH Optima of Enzymes	
Enzyme	**Substrate**	**Optimum pH**
pepsin	egg albumin	1.5
amylase	starch	4.5
urease	urea	6.7
alkaline phosphatase	β-Glycerophosphate	9.5

Source: Ref. 66

Some enzymes act in the purified state consisting essentially of protein. Many of the enzymes, however, require presence of other compounds known as co-factors. The co-factors are attached to the protein part of the enzyme. Often there is an optimum concentration of co-factors essential, such that excess co-factors can inhibit enzyme activity. Types of co-factors include metallic ions, certain anions, complex organic or metallo-organic compounds, and B-group vitamins (Ref. 66). Generally the requirement for co-factors is small and may be present as trace contamination of the substrate or picked up from the enzyme reactor equipment. The metallic cations most frequently needed are potassium, magnesium, calcium, zinc, manganese, copper, molybdenum, and cobalt. The anions most needed are chloride and phosphate.

Where there is contamination of the substrate, such that excessive quantities of co-factors are present, enzymes may be inhibited. While some enzymes require certain co-factors, the same co-factors may be inhibitory to other enzymes. Therefore, enzyme treatment would require determining and maintaining the appropriate empirical balance for reaction, and especially minimization of inorganic contamination (Ref. 66). In addition to the inhibitory effects, it is known that a small amount of inorganic salt may be necessary for enzyme proteins to be in colloidal solution; but beyond a certain concentration, salt will cause precipitation (Ref. 66).

D. EQUIPMENT AND MATERIALS

To our knowledge and that of researchers actively working in the field of enzymes (Refs. 33, 34, 35), there is no specific commercial treatment process existing today for the degradation of organics using enzymes. Only laboratory-scale degradation is reported for the breakdown of phenol, cellulose, urinous wastewater, lignin compounds and whey.

While soluble enzymes have been for purposes other than waste treatment, enzyme treatment of aqueous streams are likely to involve immobilized enzymes. The enzymes may be attached, by covalent bonding or adsorption, to nonporous supports such as glass beads or carbon. The immobilized enzymes may then be placed in a batch reactor, fixed bed or fluidized bed (Ref. 64). The fluidized bed allows more access of substrate to enzyme active sites and also minimizes clogging. Also, the use of fluidized bed allows smaller particles than would be practical for fixed bed, thereby providing relatively larger external surface areas for more enzymes to be bonded (Ref. 70). Immobilized enzymes may also be retained behind semipermeable membranes which are impermeable to the large enzyme molecule, or encapsulated within semipermeable membranes. As an example, collagen, which is a natural proteinaceous material from connective tissue, has been used successfully to immobilize about 20 enzymes; and a collagen-urease membrane has been developed in the laboratory for treating urinous wastewater (Ref. 72).

Where the waste has a high solids content, it may be less feasible to immobilize the enzymes used. In the laboratory decomposition of powdered newspapers of about 70% cellulose content, powdered newspapers, free cellulase enzymes and water are churned up in a large vat. The cellulose is totally hydrolyzed in 48 hours to glucose. Insoluble lignin, metals and inks do not appear to inhibit the enzyme process (Ref. 79). A black, sticky lignite residue remains for use as fuel or petrochemical feedstock (Ref. 71). To degrade the lignin content of the newspaper would require a separate enzyme pretreatment reaction (Ref. 64). Any metals which have become solvent and entered the glucose syrup are removed by exchange resins (Ref. 79).

III. APPLICATIONS TO DATE

There are no full-scale industrial or municipal waste treatment processes using enzymes. Outside of waste treatment, there are commercial applications of enzymes. Many of the commercial enzymes are hydrolases, which cleave bonds by hydrolysis. For example, proteases used in meat tenderizing hydrolyze proteins to smaller chains or individual amino acids. Proteases are used in the leather industry to loosen hair by hydrolysis. Lipases hydrolyze lipids to aid in digestion, as do lactases hydrolyze lactose in milk and cheese for better digestion.

At the Army's Natick Research and Development Command, scientists have spent about 30 years studying ways to protect military equipment and clothing from degradation. They have investigated 14,000 strains of fungi associated with biodegradation and found one, Trichoderma viride, especially suited for degrading cellulose. The Trichoderma viride produces cellulase for the hydrolysis of cellulose to glucose. They are currently operating a 1,000 pound of cellulose per month pilot plant. They estimate that one-half ton of glucose can be obtained from every ton of waste paper. The glucose can in turn be fermented to about 79 gallons of ethanol (Refs. 64, 71). A 1975 report on the cellulose conversion process stated that the cost of ethyl alcohol produced via cellulose conversion by cellulase would be about 33 cents per gallon. As of early July of the same year, the price of ethylene-derived ethanol was reported as about $1.00 per gallon (Ref. 64).

Many laboratories, including the Department of Agriculture's Eastern Regional Research Center in Philadelphia, and companies such as Diamond Shamrock and Corning are investigating use of the lactase enzyme (Ref. 64). At Lehigh University, a fluidized bed of immobilized lactase is being used to treat raw cheese whey. Whey is a by-product of cheese manufacturing which normally presents a disposal problem for the cheese industry. Use of the lactase enzyme can convert the lactose in the whey to its constituent monosaccharides. The Lehigh investigators estimate the annual return on investment could be 132% on a $30,000 reactor capable of handling 100,000 pounds of whey daily. They assume an immobilized enzyme cost of $10 per pound, 70% conversion of lactose to an alternative sweetener to sucrose, and 10 cents per pound price for sucrose (Ref. 70). The Enzyme Development Corporation is marketing soluble lactase. Using free lactase enzymes they project that whey solids could be 75-85% converted for 2-6 cents per pound (Ref. 64). This compares favorably with the cost of sucrose, when considering that the cost for whey waste disposal is avoided.

In the bench-scale research on treatment of urinous wastewater being conducted at Rutgers University, urease is used to split the amine group off of urea to form end-products of carbon dioxide and ammonia and potable water. The enzyme treatment is preceded by reverse osmosis to remove the dissolved inorganic salts normally present in urinous wastewater. The dual functions of salt rejection and urea conversion may eventually be used in a single vessel reactor for urinous wastewater treatment on ships, space vehicles, or in temporary settlements (Ref. 72).

Both enzyme treatment processes mentioned above convert a waste to a sugar product. Microbial systems could not accomplish the same task. Microorganisms would break down the cellulose or lactose to use the sugar for their own food; and no glucose product would be available for recovery (Ref. 79).

The above enzyme treatment applications concern relatively simple organics–cellulose, urea, and lactose. Work at the University of Pennsylvania and the Oakridge National Labs has involved degradation of a complex hydrocarbon–phenol. The UPenn group used a phenol hydroylase from yeast, and broke down the phenol to an intermediate product where the benzene ring was broken (Ref. 33). The Oakridge group conducted complete oxidation of phenol to carbon dioxide and water end-products. Both groups report the optimum application for their enzyme research is in the area of detection and monitoring (Refs. 33, 34, 68). Conventional analysis of phenol is laborious and time consuming. With developing research in enzyme purification, immobilization and co-factor regeneration, enzyme analysis may eventually be conducted continuously in an in-situ monitoring device.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements related to enzyme reaction can occur in any number of reactor designs. In a batch reactor, simple mechanical stirring may be employed with filtration or magnetic separation of the immobilized enzymes from the final effluent. A continuous flow reactor may employ stirring and ultrafiltration of the final effluent to remove free enzymes. Fixed bed or fluidized bed reactors are also used, requiring sufficient pumping pressure to pass the fluid upward through the bed. In the fluidized bed reactor, the velocity of the upward stream is fast enough to overcome gravitational force on the immobilized enzyme particles and keep them in suspension within the container. It may be necessary to aerate some enzyme treatment systems so that there is sufficient dissolved oxygen for enzymes to perform oxidation.

B. ENVIRONMENTAL IMPACTS

The principal environmental issue with enzyme treatment is that organic decomposition can be controlled such that no sludge residue remains. Unlike microbial treatment systems, there is no biomass sludge. The only residue biomass associated with enzyme treatment is formed at the enzyme production stage. Since the biomass used for enzyme production is not exposed to any harmful wastes, any sludge associated with production does not present a potentially hazardous disposal issue.

C. ECONOMIC ANALYSIS

About 8 million pounds of detergent enzymes are now being produced each year (Ref. 35). About 10 million pounds of enzymes are additionally produced annually for food and beverage industries, cheese making and medicinals (Ref. 67, 68). The production of these large quantities demonstrates that production of substantial quantities of enzymes for waste treatment is feasible. However, the cost of production is high. For enzymes to be used in waste treatment, they would have to be immobilized on an insoluble substrate to avoid being washed away with the liquid effluent. Since current enzyme treatment applications are lab scale, the production costs for enzymes such as phenol oxidase are prohibitive and cannot be applied to projecting potential treatment costs. We expect that economics would improve substantially after commercialization on a large scale.

Most of the expense with enzyme treatment is associated with enzyme production. Generally, commercial production requires capital expense for large bins to house microorganisms for enzyme production and operating expense of nutrient addition, pH control and temperature control. For enzyme use in treatment, costly purification and immobilization steps would probably be needed. Purification can involve gel infiltration, ultrafiltration, electrophoresis, centrifugation, and ultrasonic techniques. Immobilization can involve covalent bonding, adsorption, retention behind a membrane, encapsulation within a membrane, and trapping in a gel.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Enzyme treatment appears to have some potential in specialized situations. If there is no space for residual sludge disposal, enzyme treatment can treat a steady-state waste stream, such as urinous wastewater. If the objective of treatment is recovery of a decomposition by-product, the economies of waste treatment become more realistic. However, if the only objective is to decompose an organic waste stream in an economic fashion, enzyme treatment has no applicability.

The future for enzyme treatment lies in special industrial applications on a fairly steady waste composition, where the recovery of by-products such as glucose can be realized. The future also lies in special locations, such as isolated vessels for ocean or outer-space research, where continuous recycle of treated water is essential and residual sludge disposal is limited. Because of the extreme specificity of enzymes, there is also applicability for using enzymes to detect and monitor waste constituents in the environment.

The future does not lie in general waste treatment because of the sensitivity of enzymes to foreign solvent "toxic" substances.

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter VI of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

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Mr. Leo Spano, Chief of Pollution Abatement Division, Army Natick Research and Development Command (also colleagues Dr. Elwyn Resse and Dr. Mary Mandels).

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BIOLOGICAL TREATMENT:

TRICKLING FILTERS

Prepared by

Sandra L. Johnson

I. CONCLUSIONS AND RECOMMENDATIONS

The trickling filter process is a proven technology for the decomposition of organics in aqueous waste streams (less than 1% suspended solids). The process brings the wastewater in contact with aerobic microorganisms, by trickling the wastewater over media supporting the microorganisms. BOD removal efficiencies range from 50-85%.

The microbial activities of trickling filters are similar to those of activated sludge treatment. While the activated sludge system cannot tolerate shock loadings, the trickling filter is used in industry to accept shock loads and provide a relatively uniform effluent for treatment by other biological processes. The ability of trickling filters to accept variable hydraulic and organic loadings is founded in the short residence time of the wastewater in the process. Extremes in loading should, however, be avoided so that the biomass does not slough off the filter.

Trickling filters may be employed as an intermediate process in industrial waste treatment. Preceding activated sludge, trickling filters would even the load to that process in addition to removing a significant portion of the biodegradable organics.

Energy demands for the trickling filter process are low, as little as one-tenth the demand for activated sludge treatment of the same waste stream. As a result, the total costs for trickling filter treatment are slightly lower than those for activated sludge treatment. Dilute wastewaters are normally treated at total costs between 10-30¢ per 1,000 gallons, while treatment of a concentrated wastewater of 4,000 ppm BOD may cost nearly $2 per 1,000 gallons.

II. PROCESS DESCRIPTION

A. BACKGROUND

In the trickling filter process, wastes are sprayed through the air to absorb oxygen and are allowed to trickle through a bed of rock or synthetic media coated with a slime of microbial growth. The microbial slime is able to decompose organic matter in the waste stream. Process modifications employ various media and depths of media to retain the microorganisms under varying hydraulic conditions.

B. UNDERLYING PRINCIPLES

The trickling filter process relies on media support of immobile microorganisms which receive their organic substrate as waste is trickled over their cell surface. The primarily metabolic processes are aerobic, and the trickling filter system utilizes the same types of aerobic heterotrophic bacteria as the activated sludge system. In fact, in the petroleum industry, trickling filters precede the activated sludge unit and produce a continuous population of microorganisms for activated sludge treatment (Ref. 100). The aerobic microorganisms produce enzymes which perform oxidation and hydrolysis catalysis for the decomposition of simple and complex organics. Intermediate decomposition by-products, namely organic alcohols and acids, are utilized by the bacterial cells for both metabolic energy and substrate for cell synthesis. (See the discussions of activated sludge treatment and enzyme treatment elsewhere in this discussion of biological treatment processes for additional description of microbial reactions.)

The microbial slime, which coats the trickling filter media, remains aerobic primarily at its surface where air and water interface with the cells. The underlying portion, adjacent to the media, may become anaerobic. Some anaerobic decomposition results, as simple organics are hydrolyzed to organic acids, and in turn are oxidized to methane and carbon dioxide. (See the discussion of anaerobic digestion for additional description of anaerobic microbial reactions.)

Periodically, the microbial slime coating sloughs off the trickling filter media. This sloughing off may occur for several reasons. As the microorganisms grow and reproduce, the slime coating may become too heavy to remain adhered to the media. Also, as the substrate becomes limited to the underlying microorganisms, endogenous respiration becomes prevalent. Under endogenous respiration, the microorganisms become more dense and their adhesive polysaccharide cell coating diminishes.

Trickling filters decompose all types of organics, as does activated sludge treatment. Because of the relatively short residence time of wastewater contact with microorganisms, however, the percentage removal of organics is not as complete as in activated sludge treatment. Greater removals are achieved as the depth of media and the recycle ratio are increased. Trickling filters with 30 foot depth of media and recycle ratios of 3:1 are not uncommon in industry today (Ref. 159).

Trickling filters have been used satisfactorily to decompose oil and phenol. In refinery wastes 30 mg/l of oil have been effectively decomposed (Ref. 31). Trickling filter pilots of 3:1 recycle have decomposed 125 ppm phenol to 0 ppm (Ref. 159).

Trickling filters are reported to have successfully handled the following waste constituents: acetaldehyde, acetic acid, acetone, acrolein, alcohols, benzene, butadiene, chlorinated hydrocarbons, cyanides, epichlorohydrin, formaldehyde, formic acid, ketones, monoethanolamine, propylene dichloride, resins, and rocket fuels (Ref. 38). Study on the trickling filtration of nitrilotriacetic acid, which is normally used in the building of detergents, showed levels of up to 16 mg/l not harmful to the process (Ref. 21).

C. OPERATING CHARACTERISTICS

Trickling filters provide media for support of biomass, rather than having suspended biomass as in the activated sludge treatment process. The wastewater is trickled through the media and collected in an underground drain. Suspended solids, including microbial slime which has sloughed off the media, are typically clarified from the underflow.The clarified underflow may be either recycled to the trickling filter head or sent to following treatment units.

Media used in filter packing allow various process modifications. Rock media used to pack the filters typically allowed depths of 3-8 feet. The use of synthetic media allows deep filters because of their lessened tendency to clog and become anaerobic. Also, their comparatively light weight allows higher packings. Filter packings of up to 40 foot depth are reasonable where synthetic media are employed.

Hydraulic loading rates for trickling filters are generally less than 0.5 gpm/ft^2; however, loadings up to 4 gpm/ft^2 have been employed (Ref. 32). As the hydraulic loading rate increases, removal efficiency decreases. Generally, recirculation of the filter effluent improves the removal of biodegradable organics.

It appears that the short residence time characteristic of the trickling filter process allows greater variations in influent waste composition to occur without inhibiting microbial activity. The process is reputed to handle shock loadings of organic wastes, and also to be less inhibited by metals concentrations. In fact, the system is often called a roughing filter, used to level loads and reduce biodegradable organics concentrations prior to other biological treatment processes.

As mentioned above, the trickling filter process provides aerobic microbial degradation of organics. Air is entrained into the wastewater influent as it is sprayed onto the filter packing's surface. Aeration continues as the wastewater flows in thin streams over the filter media with its microbial slime. Synthetic media provide better ventilation because they can be placed with maximum spacing to avoid clogging. The extent of aeration within the filter packing is affected by the hydraulic loading rate and the influent level of organic and suspended solids loadings.

D. EQUIPMENT AND MATERIALS

The trickling filter process involves open tanks or towers to house the filter packing, and open tanks to clarify the filter effluent. Additional equipment may include recycle pumps to continuously recirculate filter effluent to the head of the process. The filter tank or tower employs a rotating spray dosing system which uniformly feeds influent wastewater to the filter surface.

As mentioned previously, the filter media may be either rock or synthetic. Rocks may be 2-4 inches long and provide a surface area of 9-25 ft^2/ft^3. Synthetic media often consist of flat or corrugated grating assembled in a criss-crossed or honeycombed manner. Synthetic media allow greater surface area; and 20-35 ft^2/ft^3 of surface area may be provided by plastic packing (Ref. 32).

No chemicals are required for the trickling filter process unless the influent wastewater stream is so nutrient poor or nutrient imbalanced that nutrients must be added.

III. APPLICATIONS TO DATE

Trickling filters have been extensively employed in the treatment of sanitary sewage. They have also been used extensively in the treatment of refinery wastewaters containing oil, phenol, and sulfide (Ref. 31). Trickling filters are essentially applicable to the same industrial waste streams as the activated sludge treatment process, including cannery, pharmaceutical, and petrochemical wastes.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Reference 60 provides methodology for the determination of electrical power consumption by the trickling filter process. Energy is needed for pumping and distributing wastewater. The energy demand of distributing wastewater over the filter surface depends upon the head loss with respect to filter depth and underdrain collection. Pumping energy requirements are based on the hydraulic head of the various process units and the recirculation ratio. For trickling filters without recycle, the power consumption is only about one-tenth that required for supplying air to the activated sludge process (Ref. 60). Less than one-tenth of the total operating costs for trickling filters is attributed to energy demand.

B. ENVIRONMENTAL IMPACTS

Trickling filters rely on microbial biodegradation of organics for processing waters. As a result, the process effluents are a liquid wastewater from which a portion of the organics have been decomposed and a biomass sludge. The sludge is similar to the biomass residue obtained from the activated sludge process.

No exotic compounds are formed from trickling filtration, and there are no gaseous emissions aside from carbon dioxide, and perhaps methane.

C. ECONOMIC ANALYSIS

Capital investment expenditures for trickling filters depend principally on the type and amount of filter media employed, with synthetic media costing more per unit volume than rock media. The amount of filter medium required is dictated by the hydraulic loading and organic loading. Influent organic loadings range from 2 to 300 lb BOD/day/1000 cu ft of media. Influent organic loadings are diluted by recirculation of filter effluent to the head of the process. Recycle ratios as high as 40:1 are sometimes required to lower the BOD applied to the filter. Eckenfelder suggests that BOD influent should not exceed 500 mg/l if aerobic conditions are to be ensured (Ref. 32).

Operating costs depend upon pumping and distribution of wastewater. Unlike the activated sludge treatment process, there is no cost for aeration.

Total costs for treating a dilute waste stream, such as sanitary sewage, normally range from 10-30¢ per 1,000 gallons for trickling filters. We have developed costs for a trickling filter system employing synthetic media to a 30-foot depth and a loading rate of about 100 lb BOD/1000 cu ft. Based on one million gallons per day of wastewater with a BOD of 4,000 ppm, a total unit cost of about $1.96 per 1,000 gallons was determined (see Table II). Figure I shows the flow diagram of process units included in the overall total cost estimate, including preliminary treatment by clarificiation, neutralization, and equalization.

TABLE 1

COST ESTIMATES FOR TRICKLING FILTERS (SYNTHETIC MEDIA)

Basis: 1 x 10^6 GPD, 10,000 ppm COD, 4,000 ppm BOD, 365 day/yr operation
Estimated Capital Investment: $2,300,000

	Annual Quantity	Cost per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor	8,760 MH	$12.00/hour	$105,000
Maintenance (2% of Inv.)			46,000
Lime	400 tons	$35.00/ton	14,000
Electricity	1.1 x 10^6 kWh	$0.02/kWh	22,000
Ammonia	330 tons	$180.00/ton	60,000
Phosphoric Acid	180 tons	$300.00/ton	54,000
Total Variable Costs			$301,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			$ 46,000
Capital Recovery (10% – 10 Years)			371,000
Total Fixed Costs			$417,000
Total Costs			$718,000
Unit Cost ($/1000 Gal)			$1.96

Source: Arthur D. Little, Inc., estimates.

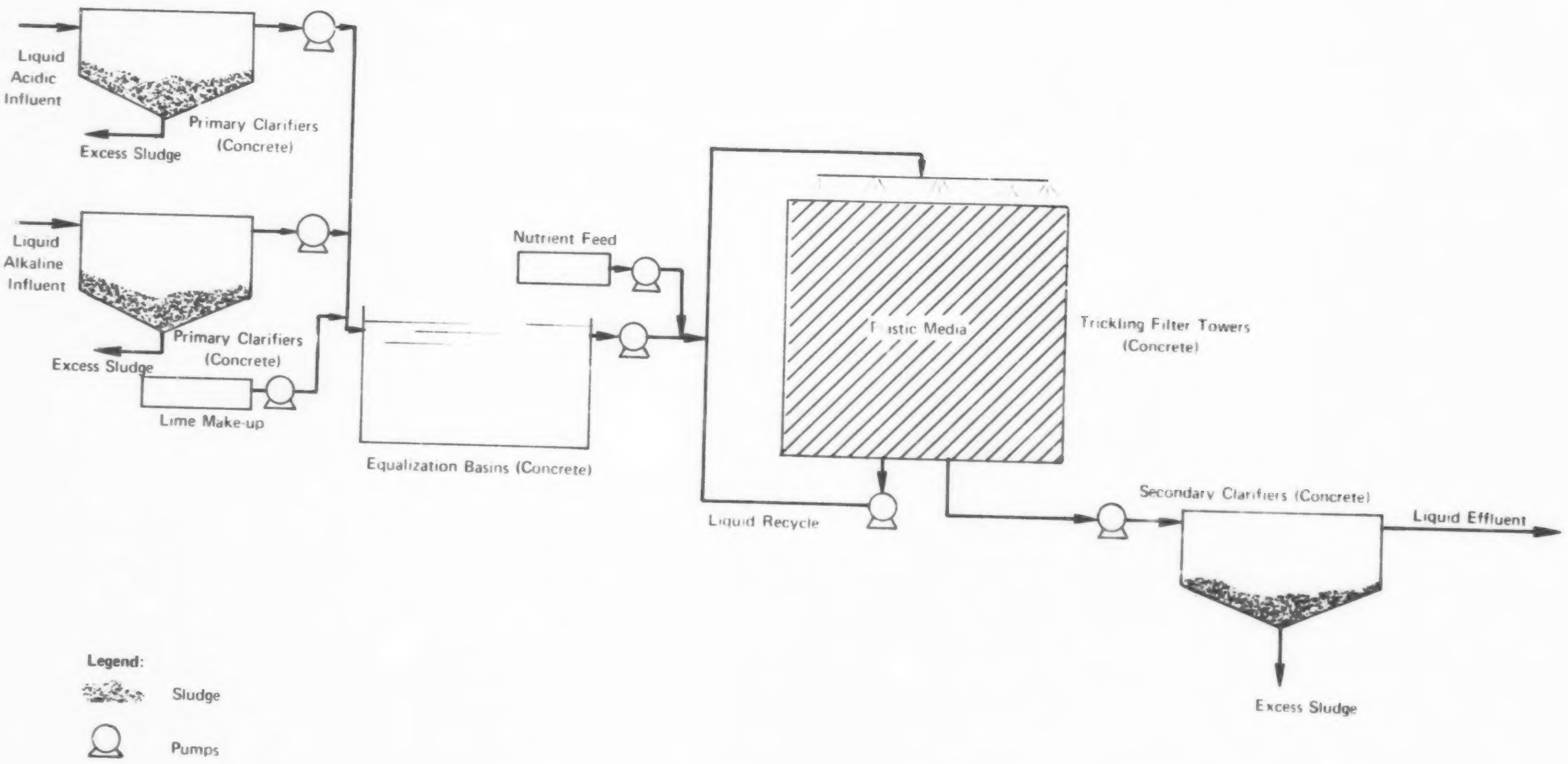

FIGURE 1 SUPER RATE TRICKLING FILTERS
COST BASIS FLOW DIAGRAM

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Trickling filter biological treatment of aqueous wastes for the biodegradation of organics is a proven technology with application to industrial waste treatment. It is principally applicable as a roughing filter which would establish relatively uniform loadings for subsequent biological processes. By placing trickling filters in sequence with activated sludge treatment, the filters could be used to even out loading variations while the activated sludge achieves high organic removal efficiencies. Even though tricking filters are more amenable to load variations than activated sludge systems, extremes should be avoided and we recommend the process be preceded by equalization.

Because of the short residence time of wastewater contact with microorganisms in trickling filters, decomposition of organics is not efficient enough to recommend this process as the sole means of biodegradation. Recycle increases the biodegradation of the influent organic loading, while also increasing the process design capacity needs.

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter VI of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

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BIOLOGICAL TREATMENT:

WASTE STABILIZATION PONDS

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

Waste stabilization ponds treat dilute aqueous waste waters (less than 0.1%solids) with low concentrations of organics. Natural biodegradation reactions are allowed to proceed as waste water passes slowly through large shallow basins, subjected to wind aeration and sunlight energy for photosynthesis. BOD removal efficiencies range from 50-90%. Although large land acreages are required, energy and chemical requirements are insignificant.

The process is more sensitive to concentrations of inorganics and suspended solids than any of the other biological treatment processes discussed in this report. Waste stabilization of industrial wastes is recommended only where the waste has received preliminary treatment to remove most of the organics, and essentially all of the inorganics. The process is recommended only as a final polishing step before effluent discharge to a receiving water body.

Total costs for treating dilute waste waters in unlined basins range from 5-15¢ per 1,000 gallons. Total costs for treating more concentrated waste streams in lined basins are nearly $1.70 per 1,000 gallons. Nearly all of the cost requirement is for capital investment amortization.

II. PROCESS DESCRIPTION

A. BACKGROUND

Waste stabilization ponds are large shallow basins which provide aerobic and facultative anaerobic decomposition of organics. The ponds rely on long retention periods and natural aeration for the aerobic microorganisms to decompose organics to carbon dioxide and water. Natural aeration is encouraged by wind action and algal photosynthesis. The facultative anaerobic decomposition which sometimes occurs in the ponds takes place at the benthic sediment-water interface.

B. UNDERLYING PRINCIPLES

Waste stabilization ponds support aerobic and facultative anaerobic microorganisms, as well as algae. There is a symbiotic relationship between the aerobic microorganisms and the algae. Algae synthesize new cells by using the sun as an energy source and by using carbon dioxide and amine as a food source. The algae provide dissolved oxygen for aerobic bacteria respiration. The aerobic bacteria hydrolyze and oxidize organics to carbon dioxide and intermediate amine by-products.

Waste stabilization pond activity varies with changes in temperature. During warm seasons, the symbiotic relationship between the aerobic bacteria and algae is most efficient. As temperatures decrease, the algae produce less oxygen. If the temperature decreases sufficiently for ice to form on the pond, both surface wind aeration and algal access to sun energy is limited. During cold seasons, facultative bacteria may shift to the anaerobic mode of metabolic activity, obtaining oxygen from selected inorganic and organic compounds. Nitrites, nitrates, and sulfates are the three principal sources of inorganic oxygen (Ref. 100). Only simple organics, such as carbohydrates and proteins, are decomposed by anaerobic microbial activity and the rate of decomposition is less than under aerobic conditions.

Anaerobic activity increases with pond depth (Refs. 156,157). With pond depths of 8-12 feet, anaerobic biodegradation of simple organics occurs at the benthic sediment/water interface. Although methane gas is produced by methane-forming bacteria (see the discussion of anaerobic digestion biological treatment for further description of microbial reactions which occur anaerobically), no odor is evident provided the aqueous medium above contains a dense algal population (Ref. 156). Both the interface of the benthic sediment, which is comprised of settled organic matter, and the top 4 inches of the sediment are actively involved in anaerobic activity, witnessed by the formation of volatile acids (Ref. 156). Increased anaerobic activity is evident in the early summer, as microorganisms digest the winter's accumulation of settled dead zoo- and phyto-plankton and bacterial cells (Ref. 156).

Since methane production is an important means of ultimate removal of carbon from a waste stream, deep ponds which promote anaerobic digestion of settled sludge may offer some advantages. Carbon dioxide, which is anaerobically and aerobically produced, is utilized by the algae and does not therefore represent ultimate removal of carbon from the system.

Waste stabilization ponds operate on more dilute waste waters than activated sludge, aerated lagoon, or trickling filter treatment processes. Since there is no mixing or aeration equipment, high suspended solids loadings are not tolerated by the process. High suspended solids loadings would settle in the quiescent waste stabilization pond environment, resulting in excessive loadings to the anaerobic benthic microorganisms and also filling of the pond.

While there may be slight bioaccumulation of trace metals in waste stabilization ponds, removal efficiencies are very low compared to activated sludge treatment. Because of the long retention times employed in waste stabilization ponds endogenous respiration leads to limited polysaccharide slime coating of the cells and therefore to limited adsorptive capacity.

Waste stabilization ponds are capable of decomposing all types of simple and complex organics. Significant decomposition of phenols in steel industry waste waters has been proven (Ref. 38), although the influent concentrations demonstrated are low, e.g., less than 1 ppm phenol. Photosynthetic algae are able to oxidize anaerobically produced sulfides and utilize the volatile acids which were anaerobically produced and not converted to methane (Ref. 164). Chlorophenols and chlorphenoxy acids have been decomposed by waste stabilization ponds; influent levels of 12 mg/l and 50 mg/l, respectively, were treated (Ref. 163).

C. OPERATING CHARACTERISTICS

Waste stabilization ponds provide quiescent retention of dilute waste water streams so that dispersed microorganisms decompose organics through their metabolic processes. No aeration or mixing is mechanically provided. Wind activity and seasonal temperature induces stratification, and turning provides aeration and mixing. As a result, the waste stabilization pond process is very sensitive to temperature and wind velocity for removal efficiencies.

Retention times for waste stabilization range from days to months. The pond depths are generally shallow so that aerobic conditions are maintained. Sunlight is essential to the algal production of oxygen, and optimum pond depths for sunlight penetration would be 6-18 inches (Ref. 32). Wind aeration coupled with algal aeration might lead to optimum pond depths of about 4 feet for fully aerobic conditions to be ensured. At depths greater than 5 feet, waste stabilization of settled sludge occurs anaerobically.

The long retention periods and shallow depths lead to large land requirements for the process. Waste stabilization is limited to rural areas having extensive acreage. Maximum organic loadings of 100-300 lb of BOD_u/acre/day are recommended by Eckenfelder (Ref. 32).

Metals concentrations appear to be more significant in waste stabilization ponds than in any of the other biological treatment processes discussed in this report. Metals inhibition is evidenced by decreased respiration of the mixed microbial population, and results in lower BOD removal efficiencies. Copper was shown to seriously affect pond performance at concentrations of 0.25 mg/l and above. Sensitivity to chromium was less, and chromium concentrations above 50 mg/l were shown to appreciably affect pond performance (Ref. 57). The investigations of copper and chromium indicated that sludge doses of these metals reacted with the natural buffering system, causing a pH depression and a significant carbon dioxide gas evolution (Ref. 57). These factors upset the delicate symbiotic relations of the mixed microbial population and seriously hampered removal efficiencies.

D. EQUIPMENT AND MATERIALS

Land, pipes, and pumps are principally all that's needed for waste stabilization ponds. Typically, the large shallow ponds are formed by moving and diking in-situ soils. For treatment of industrial processing wastes, lining the ponds with imported clay may be necessary to prevent leachate.

If the waste stabilization pond is very shallow and operates aerobically, clarification of the pond effluent may be necessary to remove the free-floating algae and suspended aerobic bacteria. It appears that temperature affects the cell coagulation abilities of algae, and that algal clarification becomes more difficult as temperatures increase (Ref. 158). Endogenous respiratory conditions prevalent in the ponds lead to biosolids which are non-flocculent and therefore difficult to clarify (Ref. 164). Deeper ponds, which allow some solids settling and anaerobic digestion, may require minimal final effluent clarification.

III. APPLICATIONS TO DATE

Waste stabilization ponds have been widely used in treatment of sanitary sewage and industrial wastes. The process is used to provide either first order biodegradation or final effluent polishing. Industries employing waste stabilization ponds are meat and poultry packing, cannery, and dairy plants; iron and steel works; paper and pulp mills and textile mills; oil refineries and petrochemical plants (Ref. 38).

One waste stabilization pond used in the poultry processing industry incorporates baffles to augment suspended solids settling. The average organic loading of the pond was 935 pounds of BOD per acre per day, and retention time was 7.35 days; 72.5% of the BOD was removed (Ref. 55). Current designs of waste stabilization ponds usually employ organic loadings of 20-100 lb BOD_5/acre/day and an average retention time of 30 days.

At the Hyon Waste Management Services, Inc., hazardous waste treatment facility, waste stabilization ponds are employed to polish the final effluent discharged from the activated sludge treatment process (Ref. 98). Average COD loadings of 400 ppm are applied, with occasional COD loadings of 2,000 ppm.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements for waste stabilization pond treatment of waste waters is minor. Energy is needed only for pumping and distribution of waste water, and gravity flow is typically employed to make that requirement insignificant.

There are no chemicals required by the process, although nutrient addition could enhance microbial activity.

B. ENVIRONMENTAL IMPACTS

A polished liquid effluent and some biomass sludge result from waste stabilization ponds. Some ponds are designed to minimize the sludge discharge, and instead encourage biosolids to settle to the bottom for anaerobic digestion. Biosolids which do escape the process are often difficult to clarify; warm temperatures and endogenous respiration respectively make algae and aerobic bacteria non-flocculent.

Gaseous emissions from the waste stabilization pond depend on the balance of the symbiotic microbial population. Typically, carbon dioxide from aerobic and anaerobic decomposition of organics is utilized by the algae. Methane gas from anaerobic decomposition is released to the atmosphere. Sulfides from anaerobic decomposition are apparently utilized by the algae. With a dense population of algae, odors are generally not detectable.

C. ECONOMIC ANALYSIS

Capital investment expenditures, excluding land costs, depend upon the earth work required and the cost of purchasing clay for pond lining. Pumping and piping costs are relatively low.

Operating costs are especially low because of the minor amount of labor, energy, and chemicals required by the waste stabilization pond systems.

Total costs reported in the literature for dilute waste water influent streams are about 5-15¢ per 1,000 gallons. These costs are mostly for amortized capital investment, as reported operating costs are often less than 3¢ per 1,000 gallons. We have developed costs for waste stabilization pond treatment of waste stream averaging 300 ppm influent BOD and one million gallons per day of hydraulic loading. Capital costs were high because of the extensive amount of earth work required to form the dikes and line the basin with compacted clay. Total costs for the process are shown in Table 1 and the flow diagram upon which the costs are based is shown in Figure 1. The costs assume the influent has received preliminary treatment by other biological process units, namely activated sludge, and that final clarification of the effluent is not necessary.

TABLE 1

COST ESTIMATES FOR WASTE STABILIZATION PONDS

Basis: 1 x 10^6 GPD – 365 Days/Year
Estimated Capital Investment: $2,250,000

Variable Costs	**Annual Quantity**	**Cost Per Unit Quantity**	**Annual Costs ($)**
Labor	3,000 MH	$12.00/hour	$ 36,000
Maintenance (2% of Inv.)			45,000
Electricity	500 x 10^3 kWh	$0.02/kWh	10,000
Total Variable Costs			$ 91,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			$ 45,000
Capital Recovery (10% – 10 Years)			$364,000
Total Fixed Costs			$409,000
Total Costs			$500,000
Unit Cost ($/1000 gal)			$1.37

Source: Arthur D. Little, Inc., estimates.

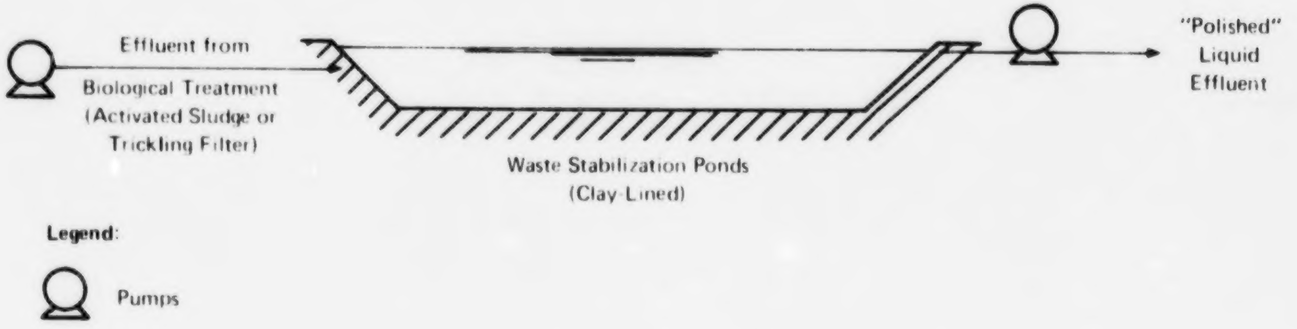

FIGURE 1 WASTE STABILIZATION POND COST BASIS FLOW DIAGRAM

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Waste stabilization ponds are recommended for polishing final effluents from other industrial waste treatment processes. The process can be employed only where climatic conditions are appropriate and available land acreages are substantial. As a final polishing step, the process neutralizes and equalizes the effluent and provides biodegradation of low organic concentrations. Toxic inorganics must be removed prior to waste stabilization ponding, because of the system's high sensitivity to inhibitors.

Because treatment facilities are known for operating variations, the use of waste stabilization ponds provides an extra insurance that final effluent guidelines limitations will be met.

VI. REFERENCES

A. LITERATURE

Literature references are included in Chapter VI of "Biological Treatment: Overview."

B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

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CALCINATION

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I. CONCLUSIONS AND RECOMMENDATIONS

Calcination is a well established process with many industrial and waste treatment applications. It is a versatile one-step process for dealing with a variety of simple or complex wastes and one of the few processes which can satisfactorily deal with sludges.

The process concentrates the waste, destroys organic components and leaves inorganic components in a more acceptable form for recovery or landfill. For many wastes the results of calcination are predictable although for complex mixtures, some pilot scale work may be desirable in order to determine how effective the process will be. If the waste contains a relatively high proportion of water, it may be desirable to pretreat by filtration, precipitation, etc., to reduce the energy requirements for calcination. Capital and operating costs are substantial, the latter associated principally with fuel requirements. If the waste contains organic components, then some or all of the fuel requirements may be supplied by in-situ combustion of the organic material.

Calcination should be seriously considered whenever a one-step process is required to deal with a complex waste, particularly if it contains both organic or inorganic components. It is likely to prove very useful whenever a landfill material of low leachability is required.

II. PROCESS DESCRIPTION

A. BACKGROUND

Calcination is the conversion by thermal decomposition at elevated temperatures of aqueous liquids and sludges into solid materials, without any interactions with the gaseous phase (such as air oxidation which occurs during incineration). For an aqueous solution, the first reaction that occurs is vaporization of the water, leaving a solid material which can be granular and free flowing, or a compacted solid. A similar process occurs in the initial treatment of a de-watered sludge (i.e., after filtration and centrifugation). In many instances it is possible to proceed further with the calcination to drive off volatile materials from the partially calcined solid, e.g. a salt, to form an oxide that will be more stable or reusable. Typical examples are the calcination of carbonates, hydroxides, sulfites, sulfides, sulfates, and nitrates to the corresponding oxides with evolution of carbon dioxide, water, sulfur dioxide, and nitrogen oxides, respectively. Organic components can also be volatilized from metal organic materials, leaving the metal as a solid residue. The resulting solid produced may be in the form of a dry granular material which is readily handled, or on heating to a higher temperature, the granules may be sintered into a solid mass. On still further heating, certain materials will melt or fuse into a glass-like material. Additives, such as silicates, borax, or phosphates, can be used to decrease the leachability of certain components in the final solid or to assist in glass formation.

Sintering (Ref. 1) can be defined as a limited form of calcination in which the physical structure, but not the chemical nature, of the solid is changed. For instance, dry powders may be heated to sinter them into a solid mass, usually with some reduction in volume. Additives such as silicates, which also sinter readily, can be added to improve this process.

B. OPERATING CHARACTERISTICS

Calcination can be a continuous process which generally operates at high temperature and atmospheric pressure. It can be applied to aqueous solutions, slurries, sludges, and tars with the objective of producing a dry powder or solid material. It can also be used for solids and powders to produce a more acceptable form of waste, i.e., one which is less soluble and therefore does not represent a leachability problem after landfill. Calcination of mixed organic/inorganic wastes can be advantageous because combustion of the organic portion will provide some or all of the heat necessary to sustain the process (calcination of a purely organic waste is generally termed "incineration" which is outside the scope of this study).

The process results in a substantial volume reduction of about 90% in the case of liquids, and 50-75% in the case of inorganic sludges. Only a minor reduction in volume occurs with the sintering or calcination of solids to drive off volatile components. In all cases, a solid material is obtained after calcination which is generally much more suitable for storage or landfill than the original uncalcined material. However, the calcine may still be toxic unless the toxic component was destroyed or was removed as a volatile material during the calcination. In the latter case, additional treatment would be required on the air or water effluents.

A major advantage of calcination is that several operations can often be carried out in a single step, i.e., concentration, destruction, and detoxification. A potential disadvantage is the fuel requirement if the waste does not contain any combustible material. Calcination temperatures are generally in the range of 650-1100°C although temperatures up to 1400°C are feasible. Above 1300°C the choice of refractory lining becomes more limited and costs increase sharply.

Calcination invariably produces particulates and gaseous products in the exit gas stream which cannot usually be emitted to the atmosphere. Some effluents may require an extensive air pollution control system. One exception is the decomposition of carbonates to carbon dioxide, which can be safely emitted to the atmosphere. However, in a number of industrial applications, it is economical to recover at least part of this carbon dioxide for recycle to the process. Particulates can be removed by cyclones, filters, or by electrostatic precipitators. Water-soluble vapor components can be removed by aqueous wet scrubbers (but the spent scrubbing liquid may require further treatment or recycle to the process to avoid potential water pollution problems). Remaining gaseous components can be removed by adsorption on carbon, alumina, silica gel, or alumino-silicates.

C. EQUIPMENT AND MATERIALS

1. Open Hearth

The open hearth calciner in its simplest form is a tray which will contain the material to be calcined. However, in this form, calcination is not very efficient because of the difficulty of exposing the material to the gas phase. Consequently, "rabble arms" are used, which rake through the material, constantly exposing fresh surfaces of the solid or sludge to the hot gases. Stationary hearths with rotating rabble arms and rotating hearths with stationary rabble arms are both used. A rotating hearth has the advantage that the solids are moved away from the feed area, thus preventing solids buildup at the feed point, and the stationary rabble arms can generally be simpler and of stronger design than the moving arms. Commercial equipment generally contains 3-12 multiple hearths stacked vertically (Figure 1). The feed is introduced at the top and is raked across each hearth by the rabble arms before falling to the next hearth to repeat the process. Several of the upper hearths are used for drying or preheating the material. The middle hearths are the hottest and complete the calcination while the lower hearths are used for cooling before discharge of the product.

2. Rotary Kiln

A rotary kiln (Figure 2) consists of a long metal tube lined with a refractory tube which can be up to 14 feet in diameter and 300-400 feet long in large industrial applications. The tube is inclined toward the combustion source which is obtained by oil or natural

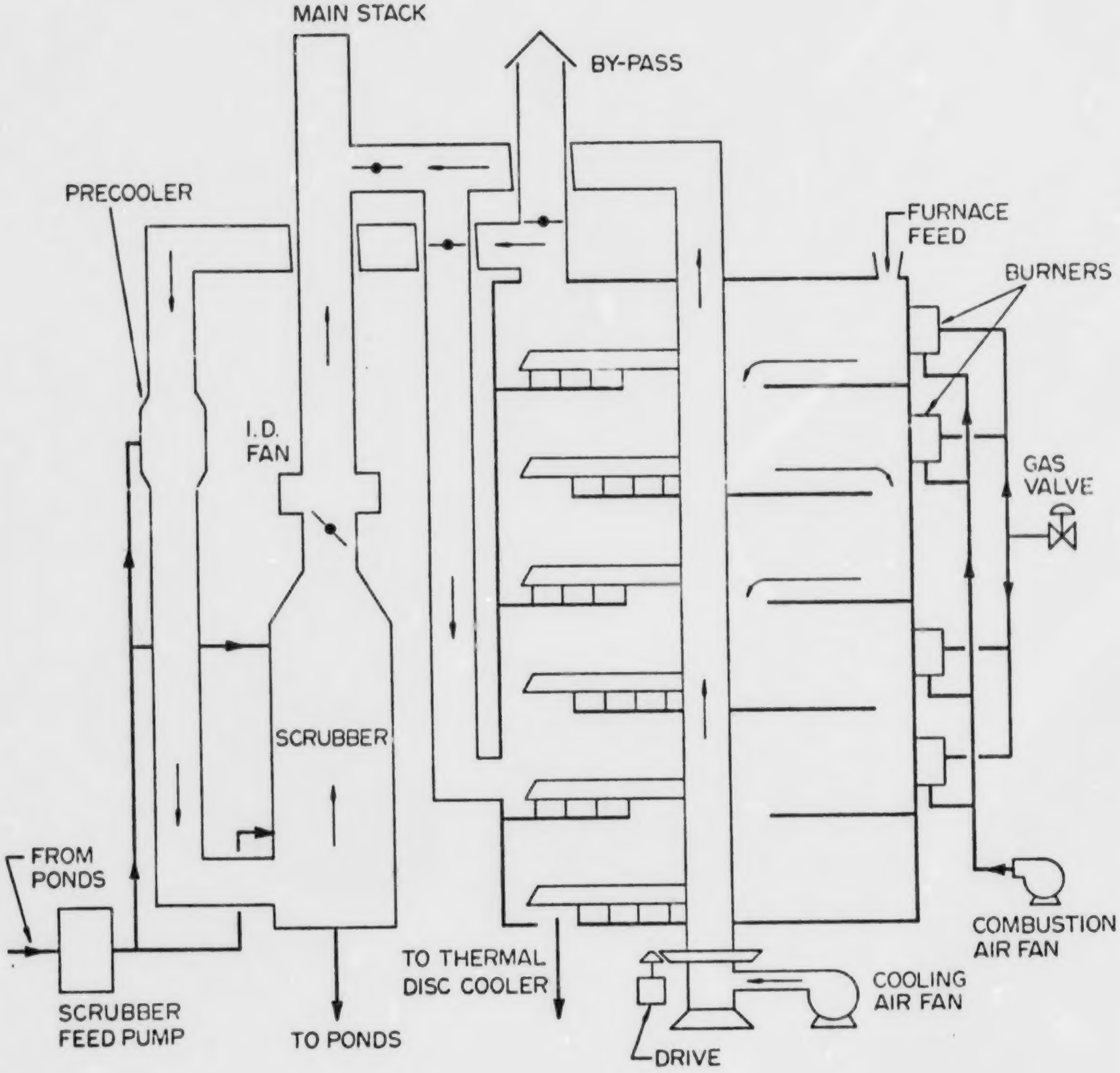


FIGURE 1 MULTIPLE HEARTH FURNACE

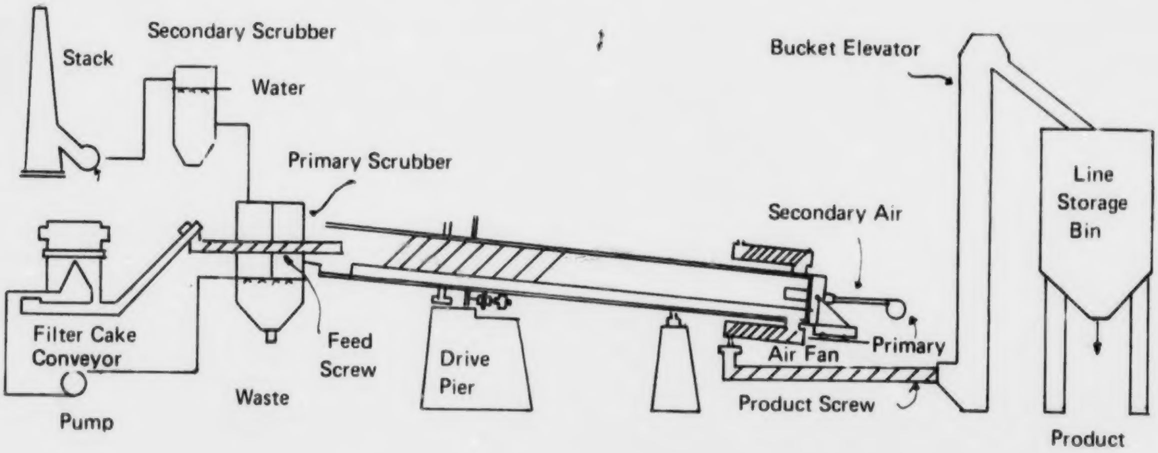


FIGURE 2 ROTARY KILN RECALCINER

gas firing. It is supported at intervals along its length and continuously rotated by an external mechanism. Feed is introduced at the cool end of the calciner at the point where the gases and vapors are evolved. Because of the continuous rotation, a high degree of turbulence, agitation and surface-to-gas contact is achieved. Lengths of chain are often installed near the feed end of the kiln to increase surface agitation and improve heat transfer. With the inclination of the calciner, the partially calcined material travels slowly down the tube while being exposed to increasing temperature and is finally discharged at the end nearest the heat source. Feed addition and product removal are continuous. Since the drive mechanism is outside the kiln, maintenance is low and there are no internal moving parts such as rabble arms, grates, or plows.

A detailed discussion of design parameters is provided in Reference 2. Optimum length:diameter ratio appears to be about 30:1. Rotation rates are in the range of 0.5-1.5 rpm and retention times 1-3 hours.

3. Fluidized Bed

Fluidized bed calcination is a more modern process which is particularly advantageous for calcining liquids and slurries. The principle of fluidization is to pass gas through a bed of small particles at a sufficient rate to impart buoyancy to the particles. This causes the bed to expand until the buoyant force of the gas flow is balanced by the gravitational force exerted on the bed particles. A simple fluidized bed calciner is shown in Figure 3. The preheated fluidizing air is introduced through multiple orifices equally spaced in the air distributor plate at the bottom of the fluidized bed. Each orifice is surmounted by a cap which helps distribute the air more uniformly and minimizes back flow of solids when the flow of fluidizing air is stopped or reduced. Operation at a superficial fluidizing velocity between 1 and 2 feet per second is generally satisfactory over beds with particle size range of 0.3 to 0.8 mm. Particle buildup occurs by deposition on smaller particles of already calcined materials, or if necessary, on inert materials which are introduced to form the fluidized bed. The material is exposed to several feet of hot bed with high turbulence and good air-to-gas contact which provides rapid volatilization of liquids and complete calcination. Caking of the bed, particularly during start-up and shut-down periods, can be avoided by careful feed and temperature control. Residence time in the bed is usually 30-60 minutes, and because the bed behaves like a fluid, temperatures are very uniform throughout. Multicompartment fluid bed calciners often are used to conserve heat and provide heat exchange between incoming feed and exit gases.

D. CHOICE OF EQUIPMENT

The three types of equipment we have described are interchangeable in many industrial applications, but for waste treatment there may be certain limitations which may make one particular type of calcination equipment more attractive. In terms of feed capabilities, the fluidized bed can handle liquids, slurries, sludges, and solids, whereas multiple hearth and rotary kiln types of equipment are probably restricted to sludges and solid materials. However, different types of feed systems are required to feed the different materials to a fluidized bed and if the waste material contains a large amount of water, it may be

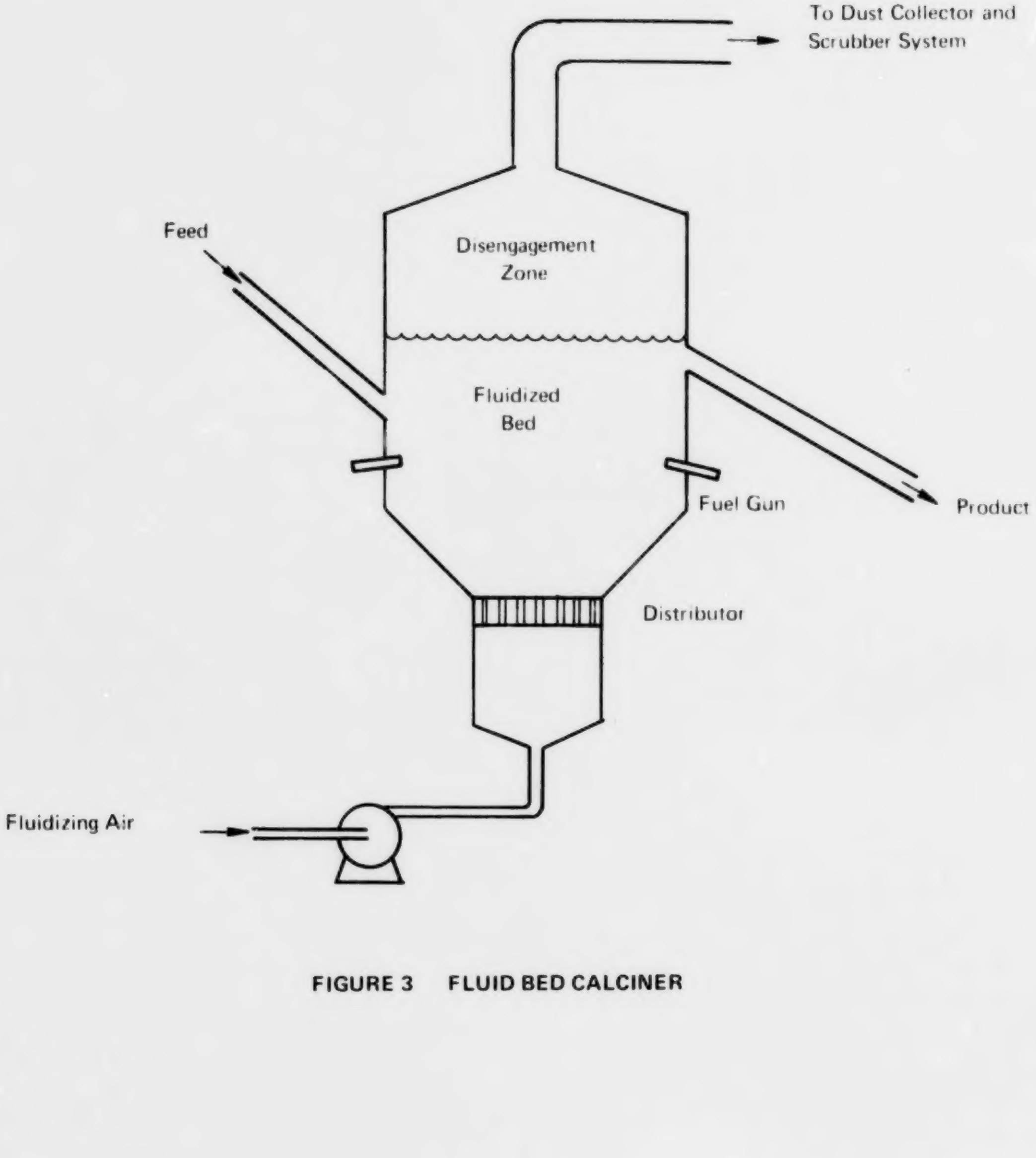


FIGURE 3 FLUID BED CALCINER

advantageous to use two fluid beds in series, the first for drying the material and the second for the actual calcination. Rotary kilns can handle higher temperatures and have a somewhat higher throughput; they are less susceptible to caking problems and can handle more variable feed compositions. They also have longer residence times than fluid bed calciners. The fluidized bed and multiple hearth are advantageous where space is at a premium. The fluidized bed is easier to seal from the atmosphere than a rotary kiln or multiple hearth, and the refractories tend to last longer. The refractory can also be made thicker in a fluidized bed or multiple hearth than in a rotary kiln which reduces heat losses. Fluidized beds provide very rapid mixing and blending of the solids, which eliminates any need for mechanical mixing and provides a high convective heat transfer rate due to the large amount of particle surface exposed to the fluidizing gas. Very close temperature regulation can be achieved by control of feed input, product discharge rates, and fuel consumption. Shutdown and start-up times tend to be short, and power and fuel costs for large diameter beds are apt to be considerably lower than rotary kilns of the same capacity in similar applications. However, for satisfactory fluid bed operations, particle shape and particle size distribution must be fairly uniform. Elongated needle-like and fibrous materials do not fluidize well. Additionally, even with near optimum particle shape, the particle size distribution is also of major importance. A high gas flow rate is required to fluidize very large particles but this can blow the fine particles out of the system. Conversely, if the fine particles are retained, then the gas flow may not be sufficient to fluidize all the large particles in the bed.

Agglomerates or wet feeds that tend to be very sticky are difficult to process in a fluid bed, whereas they cause relatively little problem in multiple hearth or rotary kiln types of equipment. The more uniform temperature in a fluidized bed may result in a lower utilization of available heat energy compared to a multiple hearth or rotary kiln if the heat losses are equivalent. The absence of moving parts in a fluidized bed lends itself to more trouble-free operation than either a rotary kiln or multiple hearth.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

Calcination has many important industrial applications. For example, this process is the basis for the production of cement, lime, magnesia, titanium dioxide, and wall plaster (Ref. 4). A modified form of calcination is also used in the smelting of ores in the form of sulfides or carbonates such as in the production of metals such as copper, lead, zinc, mercury, cobalt, iron, and nickel (Refs. 5, 6). A listing of the more important industrial applications is given in Table 1. For this report two examples are discussed below which help to illustrate the potential of calcination for waste treatment.

TABLE 1

INDUSTRIAL APPLICATIONS OF CALCINATION

Roasting of Pyrite for Sulfuric Acid Manufacture
Roasting of Zinc Sulfides for Sulfuric Acid Manufacture
Roasting of Pyrite for Gold Recovery
Arsenic Removal from Gold
Roasting of Nickel Sulfide
Roasting of Copper and Cobalt Sulfate
Oxidizing Residues for Zinc, Copper, and Nickel Recovery
Removal of Sulfur from Sponge Iron
Roasting of Copper Concentrates
Beneficiation of Phosphate Rock
Direct Reduction of Iron Ore
Treatment of Radioactive Wastes
Manufacture of Cement and Lime
Lime Recovery from Lime Sludges
Treatment of Oily Petroleum Sludges
Combustion of Spent Liquors from Wood Pulping
Reduction of Manganese Ore
Reduction of Chrome Ore
Combustion of Municipal and Industrial Sludge

1. Lime Sludges

Lime is fairly widely used to provide "softening" in water treatment. The sludge from this operation is primarily calcium carbonate with variable amounts of magnesium, aluminum, and ferric hydroxides (Refs. 7, 8). The quantity of magnesium hydroxide depends upon the magnesium hardness of the raw water and on the chemical precipitation scheme, whereas the quantity of iron and aluminum hydroxides are a function of the type and amount of coagulant used and the iron content of the raw water. A number of water softening plants recalcine this material to produce lime for reuse in the process. In spite of the additional investment, this can be economical because it reduces the need for fresh lime feed material and greatly reduces transportation costs and sludge disposal problems. In the recalcination process, the sludges are burned at temperatures of 870-1100°C to yield calcium oxide and carbon dioxide. Preliminary treatment of the sludge by appropriate de-watering techniques such as thickening and centrifugation is required; and if the magnesium content is high, a preliminary purification to reduce the magnesium content increases the value of the recalcined product. Excess magnesium can be removed by carbonation of the sludge with a stream of carbon dioxide provided from the exhaust from the calciner system, which resolubulizes the magnesium hydroxide as soluble magnesium bicarbonate.

Lime is also used as a tertiary treatment step in wastewater treatment and will be more widely employed with the enforcement of the 1983 Effluent Guidelines. The Lake Tahoe plant (Ref. 9) for recalcining lime sludges from the tertiary coagulation of municipal wastewaters has a design flow of 7.5 mgd and produces approximately 17 tons/day of lime sludge. By recalcination, the total blowdown of waste solid is reduced to about 1.5 tons/day. The cost of recalcined lime is lower than that of new lime at this specific plant, if the costs of sludge disposal are included. (Recent large cost increases for natural gas used in this plant have been compensated by corresponding increases in the purchase price for new lime.)

A flow diagram of the multiple hearth recalcination furnace and associated equipment is shown in Figure 4. Lime mud is pumped from the chemical clarifier and recarbonation reaction basin to a gravity thickener. Thickened lime mud is then pumped to solid-bowl concurrent-flow centrifuges. The sludge also contains the phosphorus removed by the tertiary treatment in the form of insoluble hydroxyapatite so recovery at the centrifuge is limited to about 80% of the total solids which eliminates most of the hydroxyapatite from the calciner feed.

The cake from the first centrifuge (about 45-48% solids) is carried by a belt conveyor to a 14.3 foot diameter, 60 foot high, six-hearth furnace for calcination. Its capacity is 10 tons/day. The top two hearths dry the sludge at 315-425°C and the next three are the effective recalcination hearths operating at about 980°C. The bottom hearth is used to cool the product before discharge. Recalcined lime is conveyed out of the furnace by gravity through a crusher to a thermal disc cooler where lime temperatures are lowered from 371°C to 37-65°C, through a rotary air lock, and then is pneumatically conveyed to a 35-ton capacity recalcined lime storage bin. Stack gases are scrubbed in a multiple tray scrubber before being exhausted to the atmosphere. A portion of the gases are recycled to the recarbonation system where CO_2 is absorbed to adjust the pH of the lime coagulated wastewater to about 7.

The optimum calcination temperature appears to be 980°C. An increase to 1040°C only produces about 5% more available calcium oxide and little improvement in the slaking rate. To avoid agglomeration and to assure destruction of all organic material, the minimum temperature would be 870°C. Recalcined lime is more like talc than fresh lime and does not flow as readily under gravity. This can cause problems if the feed bins are not carefully designed.

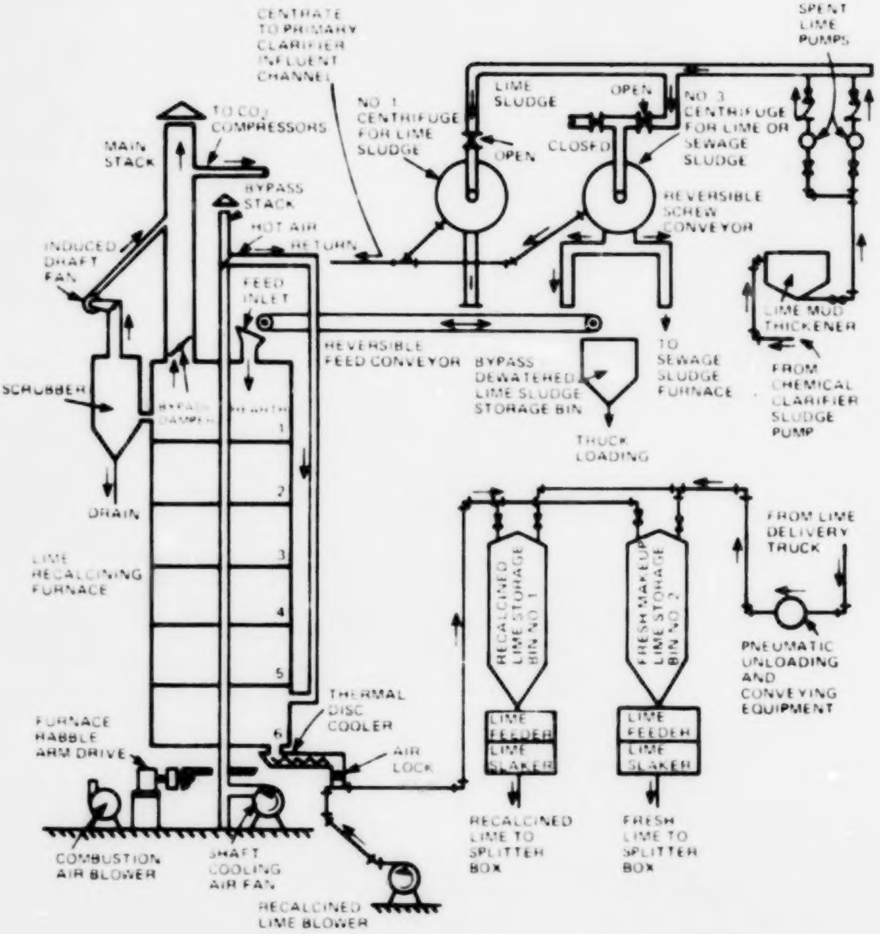


FIGURE 4 THE LIME RECALCING SYSTEM AT SOUTH LAKE TAHOE

Multiple hearth furnaces recently constructed at the new Central Contra Costa County waste treatment plant (Refs. 10-12) will calcine sludges resulting from lime coagulation of raw wastewater. The furnaces are 22 feet in diameter with eleven hearths designed to process 150 tons/day of sludge. Sludge from the primary settling stage is centrifuged to recover about 50-55% of the solids which recaptures most of the lime while rejecting other constituents such as magnesium and phosphorus. During extended pilot plant studies it was found that silica tends to build up on recycle and this may cause problems in extended plant operation.

Fluidized beds are also widely used for lime sludge calcination (Refs. 13, 14). A flow diagram for a commercial fluidized bed system is shown in Figure 5. Lime mud filter cake is fed into a paddle mixer along with dry recycled fines and quench water. The mixture then goes to a cage mill disintegrator where precooled calciner stack gas at 537°C dries and disintegrates the moist solids. The resultant dry carbonate is conveyed by the exhaust gas to a cyclone separator. Large fraction discharge from the cyclone is split, a portion being recycled to the mixer and a portion to the calciner feed bin. Calcination takes place in a two-compartment fluidized bed furnace. The upper fluid bed of the reactor is used for low temperature calcination (815-870°C) of calcium carbonate and the pelletization of calcium oxide. The lower fluid bed cools the calcined product. Lime produced by this system is in the form of pelletized particles, 6 to 20 mesh in size, which are "soft-burned," dust-free, highly reactive, and more easily handled than the lime dust obtained with a multiple hearth furnace.

2. Petroleum Residues

Calcination is used by the petroleum refining industry for the treatment of heavy residues and tars with the formation of a solid coke and production of gaseous and liquid materials which have an enhanced economic value. Two major coking processes are in use today, delayed and fluid coking (Refs. 15, 16). Delayed coking is a semi-continuous process in which the heated charge is transferred to large soaking drums which provide the long residence time needed to allow the cracking reactions to proceed to completion. The feed in these units is normally an "atmospheric" petroleum residue, although cracked tars and heavy gas oils may also be used. In continuous operation (Figure 6a) two drums are used with one on-stream while the other is being cleaned. The temperature in the coke drum varies from 415-450°C at pressures of 50-90 psig. Lighter cracked products leave from the top of the drum and the coke deposits form on the inner surface. After about 24 hours, the drum becomes filled with porous coke. It is then cooled to permit removal of the coke by multiple high-pressure water jets.

In fluid coking (Figure 6b), the hot tar is sprayed into a fluidized bed of hot fine coke particles. Use of a fluid bed permits the coking reactions to be conducted at higher temperatures and shorter contact times than can be employed in delayed coking, resulting in lower yields of coke and larger quantities of liquid products. Fluid coking uses two vessels, a reactor and a burner. Coke particles are circulated between these two vessels to transfer heat

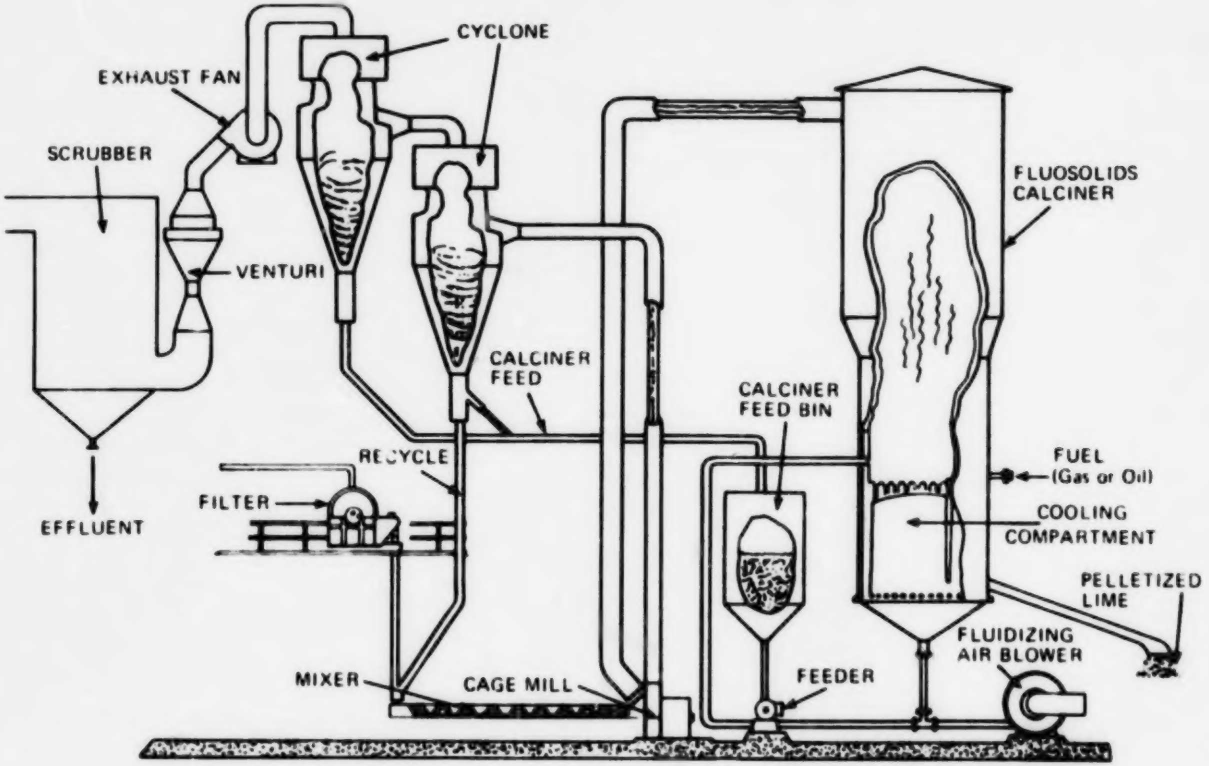
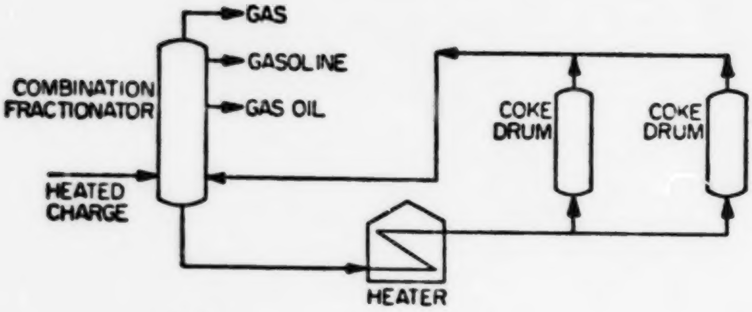
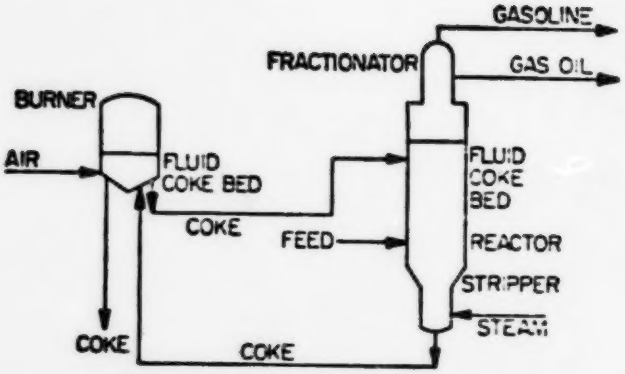


FIGURE 5 FLUIDIZED BED SYSTEM FOR LIME RECALCINATION



(a). Delayed coking.



(b) Fluid coking.

FIGURE 6 COKING OF PETROLEUM RESIDUES

to the reactor and this heat is generated by burning a portion of the coke. The temperature in the coking vessel ranges from about 480-565°C at atmospheric pressure and the incoming feed is partially vaporized and partially deposited on the fluidized coke particles. Steam is usually introduced at the bottom of the reactor to help fluidize the bed. No preheat furnace for the feed is required since the circulating coke particles supply the necessary heat for the coking reaction and thereby control the reactor temperature. The hot pitch on the particle surface cracks and vaporizes, leaving a residue which dries to form coke. The vapor products then leave the bed and pass through cyclones which remove most of the entrained coke.

B. CURRENT APPLICATIONS TO WASTE TREATMENT

1. Radioactive Wastes

Treatment of liquid radioactive wastes by various forms of calcination has been practiced for a number of years in order to produce solids containing the radioactive component in a concentrated form which can be easily and safely stored. A brief description of some of these operations follows.

Fluidized bed calcination has been employed at the Idaho Chemical Processing Plant since 1963 for solidifying high level liquid radioactive wastes resulting from the reprocessing of highly enriched aluminum/uranium and zirconium/uranium alloy fuels at that plant (Refs. 17-20). A flow diagram of the operating facility is shown in Figure 7. The waste streams consisting of aluminum nitrate/nitric acid and zirconium fluoride are injected directly into the calciner (85-140 gal/hr) through atomizing nozzles where they impinge on a bed of granular solids. The solutions cannot be concentrated (beyond about 5%) by evaporation because crystallization occurs and creates handling problems. Combustion of an oxygen/kerosine mixture maintains the bed at 500°C. Thermal decomposition of the nitrate and fluoride salt solutions to metallic oxides and fluorides, releasing water vapor and nitrogen oxides, are the principle reactions occuring during calcination. Addition of calcium nitrate to the solution prevents evolution of fluorides in the off-gases by the formation of calcium fluoride. Effective removal of radioactive components from the off-gases is necessary. and an extensive gas treatment system is employed for this purpose. Liquor from the wet scrubber is recycled to the calciner feed.

At Hanford, cesium and strontium are recovered from the supernate and sludge of aged alkaline wastes from acidic wastes (Ref. 21). The residual wastes are neutralized, stored for 5-7 years, and combined with older waste concentrates and aluminum wastes for final evaporation to form salt cakes.

Spray solidification (Ref. 22), pot calcination (Refs. 23, 24), and phosphate glass solidification (Ref. 25) have all been demonstrated with radioactive wastes at the waste solidification engineering prototype at Hanford. The "Fingal" process (Ref. 26) developed in the United Kingdom produces a glass-like material by mixing the concentrated liquid waste with silica/borax slurry and calcining at a temperature of 1,050°C. This process has

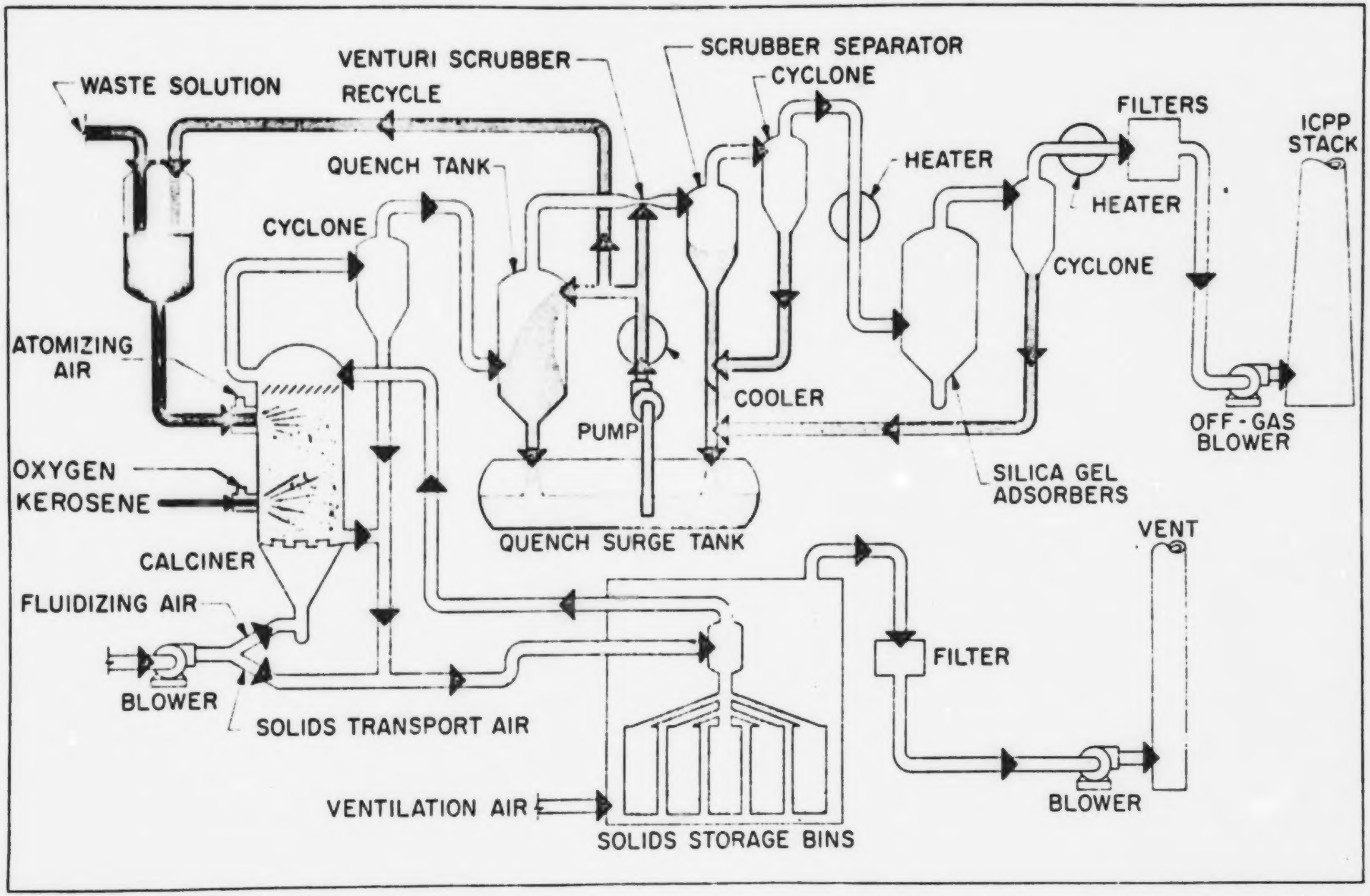


FIGURE 7 FLOWSHEET OF THE WASTE CALCINING FACILITY USING INBED COMBUSTION FOR HEATING

been taken through the pilot plant stage. Other calcination processes that produce a glass have been developed in France (Ref. 27) and in the Soviet Union (Ref. 21).

Aerojet Energy Conversion Company has developed a radioactive waste management treatment that reduces the volume of waste to be stored by conversion of all liquid wastes into anhydrous calcined solids which are subsequently encapsulated in the proprietary solidification agent (Ref. 28). The volume of liquid wastes is reduced by a factor of 10-20 and the volume of spent resins and sludges by a factor of 2-4 when compared with other solidification methods. The process is based on a fluid bed calciner; lower capital costs, lower operating costs, and reduced radiation exposure of personnel are claimed in comparison to other solidification systems.

2. Refinery Sludges

A large fluid bed calciner at the Amoco Refinery in Whiting, Indiana, processes 370 tons/day of wet sludge containing 85-95% water (Refs. 29, 30). This waste is a combination of sludges from flotation clarifier skimmings, API separators, tank cleanings, biological treatment, and spent caustic. In addition to hydrocarbons, the sludge contains compounds of Ca, Mg, K, Na, S, Fe, Al, and phosphates. The seed particles are mainly aluminum oxide (derived from alum used in water treatment) and the bed temperature is maintained at 720°C to avoid melting the bed product which has a complex analysis (see Table 2). If the sodium and chloride content becomes too high, melting and agglomeration may occur in the bed. This can be overcome by the addition of clay which reacts with the various components to form high melting alumino-silicates.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

The EPA has sponsored a pilot study of spray calcination of sulfuric acid wastes from titanium dioxide manufacture (Ref. 31). The primary objective was to recover sulfuric acid for recycle to the manufacturing process, but the waste stream contains substantial quantities (10-15 wt. %) of metal sulfates (iron, aluminum, magnesium, vanadium, chromium and manganese). This process overcomes most of the corrosion problems associated with earlier recovery processes and produces 85% sulfuric acid and free flowing dry solids in the form of anhydrous metal sulfates. The solids are highly water soluble and are not suitable for landfill in this form. In addition, they contain free acid due to occlusion and formation of a relatively stable double salt of $Al_2(SO_4)_3$ and H_2SO_4. Schemes for further calcination have been proposed which decompose the metal sulfates to insoluble metal oxides with the recovery of sulfur dioxide (Ref. 32).

Abstracts from SWIRS (Refs. 33, 34) give information on some Japanese work where calcination was applied to sludges from chromium plating processes containing calcium, nickel, and copper, in addition to chromium. Sodium silicate or kaolin clay were added as stabilizing agents in amounts of 10-30% and the material was calcined for 1 hour at 800-900°C. It was found that the leachability of heavy metals from the clay-stabilized materials was very low. Similar work on calcination of plating sludges containing primarily zinc and copper has been carried out in Switzerland (Ref. 35). It was found that calcination temperatures over 1000°C were required in order to attain virtually insoluble products. Addition of broken glass gave a product with a smooth non-porous surface which resisted weathering although its leachability was very similar to the untreated material.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Calcination requires a substantial energy input which is expended in two ways: first, to remove any remaining water and, second, to convert the dry material into a more refractory form by heating at a relatively high temperature (1090°C). Calcination of dry material usually requires only 1-3 million Btu/ton solid product but a sludge containing only 10% solids will require about 20 million Btu/ton of solid product. Obviously, pretreatment of dilute sludges or solutions by filtration or precipitation, etc., is advantageous in that it greatly reduces the energy requirement for subsequent calcination. Many inorganic sludges after filtration or centrifugation reach 50-60% solids.

Energy requirements are also reduced if the waste material contains an organic fraction which is combusted during the calcination step. For example, an organic content of 20-30% will supply most of the heat necessary for calcination of a sludge containing 50-60% water.

B. ENVIRONMENTAL IMPACTS

Calcination generally gives a product that is suitable for disposal to landfill or for recovery. A large volume reduction is achieved and calcined products typically show low leachability of hazardous components. Additional air emissions are invariably produced during the process. In the case of hydroxides and carbonates, these emissions are innocuous and can be discharged to the atmosphere. Carbon dioxide emissions from lime recovery are often recycled as part of the process. However, to remove hazardous components from the gaseous effluent, fairly extensive air treatment systems must be employed, including filters or cyclones to remove particulates, wet scrubbers, and possibly final adsorption systems for remaining gaseous components. Therefore, if hazardous components are volatilized, the costs of calcination may be increased substantially. Nitrogen oxides may be produced during fuel combustion. Treatment of the spent scrubbing liquid from wet scrubbers may also be necessary, but this can be recycled to the calcination step. Fine particulates captured in the cyclones are also recycled. Some air emissions can be eliminated by the addition of suitable materials to the calciner feed; for example, addition of calcium will tie up fluorides as calcium fluoride. Similarly, clays can be added to the feed which react with the hazardous components to form complex alumino-silicates from which the hazardous component has a very low leachability.

C. ECONOMIC ANALYSIS

Capital and operating costs are very sensitive to the concentration of the material being [illegible]ed. In particular the removal of water from dilute aqueous solutions will result in a [illegible] energy cost.

Investment costs are very sensitive to the material being treated. Taking lime recalcination as an example, investment costs for a rotary kiln are $10-20 thousand per daily ton (including installation) and for a fluidized bed or multiple hearth $15-30 thousand per daily ton. Operating costs are mainly for fuel and power since little labor is required. One operator can usually take care of two or three units. Estimated capital and operating costs, based on the flow diagram in Figure 5, are shown in Table 2. Total cost is about equally divided between capital* and operating cost, and, for this estimate amounts to 2.15¢/lb of solid recovered. This is a relatively small cost if the product can be recycled. It does not take any credit for the virtual elimination of disposal costs. The example does not assume any heat recovery from combustion of organic materials in the waste, which can have a marked effect in reducing operating costs.

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* N.B. Capital costs in the example quoted include the costs for filtration which is a separate unit operation and also all the costs associated with the air pollution control equipment.

TABLE 2

ESTIMATED COSTS FOR CALCINATION

Basis: 6,500 gal/hr at 10% solids, (6000 lb/hr solids) 350 days per year
Capital Investment: $2,900,000[1]

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor	8,500 hr	$12.00/hr	102,000
Maintenance (3% of Inv.)			87,000
Utilities			
Electricity	5.71×10^6 kWh	$ 0.02/kWh	115,000
Fuel	63×10^9 Btu	$ 2.25/10^6 Btu	142,000
Water	5.25×10^6 Gal	$ 0.40/10^3 Gal	2,000
Total Utilities			259,000
Total Variable Costs			448,000
Fixed Costs			
Taxes and Insurance (2% of Inv.)			58,000
Capital Recovery (10%-10 yrs)			474,000
Total Fixed Costs			532,000
Total Costs			980,000
Unit Costs ($/$10^3$ gal of waste treated)			17.95
(¢/lb of solids recovered)			¢ 2.15

1. Includes the capital costs for filtration and the capital costs associated with the air pollution control equipment.

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. CLASSES OF WASTES THAT CAN BE HANDLED

Calcination can be used for organic and organo-metallic compounds, particularly in the form of residues, tars, or sludges where the organic component can be either partially or completely volatilized or converted to a solid form. It can also be applied to inorganic salts that contain a volatile component. Examples of such salts are: hydroxides, carbonates, nitrates, sulfites, and sulfates. Calcination is particularly useful as a one-step process for converting a mixed organic inorganic waste to more acceptable products.

B. OPERATIONAL PRACTICALITY

Calcination has been widely used in industrial and waste treatment applications. Suitable equipment in the form of rotary kilns, multiple hearth calciners, and fluidized bed calciners is commercially available from a number of manufacturers. Calcination destroys toxic organic components (and some inorganic components, e.g., CN, S, SO_3). It concentrates the waste and converts it into a form which is more acceptable for recyle or for landfill.

C. ECONOMICS

The capital investment and operating costs will be strongly influenced by waste composition. If large quantities of water must be vaporized from a dilute solution, then the most critical parameter may be the amount of fuel required to provide the necessary heat energy for complete calcination. Conversely, the presence of organic components will supply a heat energy "credit" which will reduce operating costs.

D. POLLUTION POTENTIAL

Calcination is very effective in reducing the volume of waste for land disposal and in producing a more stable waste form where the hazardous components are not readily leached from the final waste material. Organic components are completely destroyed.

With some wastes, the process has the potential of producing substantial air emissions which must be treated to remove particulates and toxic vapors. If wet scrubbers are used it may be feasible to use the process feed as the scrubbing liquid or recycle spent scrubber effluent to the process.

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CATALYSIS

Prepared by

Douglas Shooter

I. CONCLUSIONS AND RECOMMENDATIONS

Catalysis is essentially applicable to all types of organic compounds including hydrocarbons containing halogens, nitrogen, oxygen, sulfur, and phosphorus. It is also applicable to oxidation and reduction reactions involving heavy metals, the oxidation of cyanides, carbonyls, and sulfites. Catalysis should be considered for waste treatment when a chemical transformation process has been shown to be applicable or when the chemistry of the components in the waste stream indicates that a chemical transformation is possible. If the transformation can be successfully catalyzed, lower operating costs and lower energy costs can be anticipated.

Many industrial processes are based on catalysis and present investigations have shown promising applications to waste treatment although few, if any applications are operated commercially at present. Catalysts are extremely versatile; they can provide selective detoxification as in the dechlorination of chlorinated pesticides or can provide complete destruction as in the air oxidation of cyanides. Further work should be supported to extend the range of these investigations and to demonstrate commercial feasibility of those which look most promising.

II. PROCESS DESCRIPTION

A. BACKGROUND AND UNDERLYING PRINCIPLES

Catalysis does not describe a process; it is a modification to any one of the chemical transformation processes. A catalyst is an agent which alters the rate of a chemical transformation process but is chemically unchanged at the end of reaction. It is neither destroyed during the processing nor incorporated into the product. Catalysts present in much smaller concentrations than the stoichiometric amounts required to complete the reaction can alter the rate of a chemical reaction by orders of magnitude. Catalysis has no influence on the thermodynamics of a particular process. The equilibrium point is still the same, only the rate of approach to equilibrium is changed because the catalyst will act to speed up the rate of reaction to the same degree. However, if several parallel or consecutive reactions are involved, the end products may be altered because one reaction path is preferentially catalyzed.

B. OPERATING CHARACTERISTICS

Catalytic Reactions are conveniently divided into two general types which are defined under the headings below.

Homogeneous catalysis occurs when all the reactants are contained in a single phase. The primary groupings in this category are reactions between gases and vapors that are catalyzed by other gases and vapors, and reactions in a liquid medium containing a liquid catalyst or a catalyst in solution. The term is also used when one of the reactants is a gas and the other reactants and the catalysts are in another phase, since experience indicates that as a result of the solubility of the gas, the transformation takes place throughout the liquid and not at the liquid-liquid interface.

Heterogeneous catalysis consists of transformations of multi-phase systems containing at least one solid phase which is generally the catalyst, or at least a kinetically active component of the catalyzed system. The most important common examples of heterogeneous catalysis are those in which gaseous or liquid reaction systems are placed in the presence of a solid catalyst.

It is possible to make generalizations about the type of catalysts available for conducting a specific type of reaction (Table 1) although it is much more difficult to predict the precise behavior of a particular catalyst reactant system. However, the literature on catalysis is voluminous, covering every conceivable type of chemical reaction, and analogies can be drawn between these reactions and the treatment of hazardous wastes with similar chemical functions. The General Bibliography in Section VI provides a more extensive introduction to the field.

TABLE 1

A CLASSIFICATION OF HETEROGENEOUS CATALYSTS ACCORDING TO THEIR PRINCIPAL FUNCTIONS

Class	**Metals**	**Metal Oxides and Sulfides**		**Salts and Acids**
Conductivity Type	**Conductors**	**Semi-conductors**	**Insulators**	–
Functions	Hydrogenation Dehydrogenation Hydrogenolysis (oxidation) (reduction)	Oxidation Reduction Dehydrogenation Cyclization (hydrogenation)	Dehydration Isomerization (hydrogenation)	Polymerization Isomerization Cracking Alkylation Hydrogen Transfer

Source: Ref. 2

Catalysis can be applied primarily to single phase liquid systems and vapors although slurries can be treated in stirred tank reactors if a homogeneous catalyst is used or if subsequent separation of catalyst and solid is inconsequential. Catalysis would not normally be applicable to sludges, tars, or solids without preliminary treatment to bring the material into a more acceptable form.

After catalytic treatment the toxic component would be destroyed or converted into a more acceptable form. Since catalysis is generally quite selective, all toxic components in a complex waste may not be destroyed in a single operation.

There are no specific limitations on operating conditions, but the advantage of a catalyst is that by increasing rates of reaction it allows the treatment to be carried out under less severe conditions of temperature and/or pressure than the equivalent non-catalyzed transformation.

C. EQUIPMENT AND MATERIALS

There are three types of reactors used for catalytic reactions. These are the stirred tank reactor, the fixed bed reactor, and the fluidized bed reactor. The stirred tank reactor is invariably used for homogeneous catalyzed reactions, and also for heterogeneous reactions in the liquid phase which are catalyzed by a finely divided catalyst slurry. The fixed bed reactor is usually characterized by a tubular reactor containing a solid catalyst in the form of particles from about 1/8-inch to 1-inch in diameter which may be irregular, spherical, cylindrical, or annular rings. Fixed bed reactors are widely used for vapor phase reactions, liquid phase reactions, or mixed phase reactions in what are commonly called trickle flow reactors. In a fluidized bed reactor, very finely divided catalyst particles are kept in uniform suspension by the fluid flow to provide a constant condition for fluid and catalyst particle interactions throughout the reactor. The fluidized bed reactor is completely mixed and hence, is similar in operation kinetically to a stirred tank reactor for liquid phase reactions. Because of the even heat distribution, fluidized beds are particularly advantageous for highly exothermic reactions.

III. APPLICATIONS TO DATE

A. PRINCIPAL CURRENT APPLICATIONS

Catalysts are used in many industrial applications. Some of the more important are indicated below. Further information can be obtained by reference to the general bibliography. The petroleum industry uses heterogeneous catalysts extensively for conversion of hydrocarbons in various crude oil fractions and for purification of crude oil fractions. Specific process applications are catalytic cracking, catalytic hydrocracking, reforming, hydrogenation, hydrodesulfurization, and polymerization.

The chemical industry also uses catalysts in a large number of heterogeneous and homogeneous processes. Examples of homogeneous reactions are polymerization of olefins, hydroformylation of olefins to aldehydes, and oxidation of olefins. Examples of heterogeneous reactions are the synthesis of ammonia, methanol, formaldehyde, and organic intermediates such as ethylene oxide, and acrolein. Other catalytic reactions carried out in the chemical industry include oxidation, reduction, polymerization, hydration, dehydration, and hydrolysis. Catalysts are used in the pharmaceutical industry for hydrogenation and oxidation of chemical intermediates, and in the textile industry for the curing of special finishes which impart water repellancy and wash and wear characteristics to textile fabrics.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

1. Catalytic Oxidation

Catalytic oxidation is quite widely used (Refs. 1-3) as an alternative to thermal incineration for the decomposition of waste organic materials. The process is commonly mis-named catalytic combustion or catalytic incineration in spite of the catalytic features which make it theoretically and practically different from combustion or incineration. Nevertheless, this particular process is being treated in a separate program and will not be discussed further in this report.

2. Destruction of Pesticides

Several reports describe work on the use of catalysts to destroy or detoxify chlorinated pesticides. A U.S. patent to Sweeney & Fisher (Ref. 4) describes the use of various metal combinations for the destruction of chlorinated organic pesticides. All the examples in the patent except one refer to DDT, but the following compounds are also claimed to be decomposed: toxaphene, chlordane, dieldrin, endrin, eldrin, heptachlor, and polychlorinated polyphenols. Preferred catalyst "couples" were zinc/copper, iron/copper, and aluminum/copper, but other catalysts such as zinc/silver, magnesium/copper, and cadmium/copper also showed substantial activity.

The metallic couples described as catalysts for detoxification of chlorinated pesticides are prepared by depositing a thin film of catalytic metal such as copper or silver, upon a metal reductant such as zinc. They may also be prepared in the form of an alloy. For example, the zinc/copper couple is formed by adding an aqueous solution of cupric chloride to an acetone suspension of technical grade zinc dust. The best results were obtained with a copper-to-zinc wt. ratio of about 1:33. This suspension of the zinc-copper couple is then acidified to 0.5 normal with acetic, sulfuric or hydrochloric acid (pH 1.5-4.0) and reacted with DDT at 25°C on a one-to-one weight basis. Data were obtained on an emulsifiable concentrate of DDT in water typical of DDT plant wash effluents. The zinc/copper couple reduced the DDT concentration from 421 ppm to 1 ppm after one hour at 75°C. Complete removal of chlorine was not achieved, the primary reaction product was 1.1 bis-(p-chlorophenyl)-ethane which is much less toxic than DDT. The reaction with an aluminum/copper couple also reduced the DDT but gave a different reaction product from the zinc/copper catalyst. Most of the product was in the form of an insoluble precipitate, and from analysis it was concluded that this material was essentially a dimer of DDT formed by the loss of two chlorine atoms.

Work sponsored by EPA on the dechlorination of a variety of pesticides is also under way at Worcester Polytechnic Institute (Ref. 5). Screening experiments using palladium, platinum, and nickel catalysts supported on alumina have shown that DDT, arochlor (pcb), aldrin, dieldrin, and toxaphene can be dechlorinated. The dechlorinated hydrocarbon 1-1 biphenyl ethane is produced with high selectivity although some chlorinated intermediates were also present. Vapor phase experiments were conducted at 210-240°C using 10% Pd/carbon with hydrogen at 19 psig.

Liquid phase experiments showed that complete dechlorination could also be obtained under less severe conditions (room temperature and pressure conditions). Nickel catalysts – nickel hydroxide, or nickel on kieselguhr, reduced at 360°C in hydrogen – have also been investigated. DDT, dieldrin, and aldrin dissolved in ethanol and NaOH (to act as an acceptor for Cl) was successfully reduced in the liquid phase, but under more severe conditions (100°C, 750 psi) than with the palladium catalyst. Attempts to replace the ethanol solvent with xylene and the sodium hydroxide were unsuccessful.

Another approach to catalytic dechlorination of pesticides has been adopted by Dennis and Cooper at the U.S. Army Medical Bioengineering Laboratory (Refs. 6, 7). They have been investigating catalytic methods for the destruction of small quantities of chlorinated pesticides in the field, residues, and unused pesticide solutions by relatively inexperienced personnel without any special equipment. Their preferred catalyst for the dechlorination of DDT is nickel boride, a black solid prepared in situ by the reaction of sodium borohydride with an alcoholic solution of nickel chloride. Decomposition of the sodium borohydride produces the hydrogen for reaction. Under these relatively mild reaction conditions, most of the DDT was destroyed; but a variety of chlorinated intermediates was obtained and very little of the completely dechlorinated product was made. Other catalysts, cobalt, manganese, and iron were also tried but were found to be less active than nickel. Several other chlorinated pesticides were also studied with the following results:

1. Heptachlor and chlordane are only dechlorinated to a minor extent under room temperature conditions giving predominantly the pentachloro compound.
2. Lindane is completely dechlorinated to benzene and cyclohexane products.
3. 2.4.D and 2.4.5.T are completely dechlorinated to the phenoxy acetic acids.
4. Aldrin and dieldrin do not dechlorinate readily losing effectively only one chlorine atom by this procedure and forming degradation products which are still very toxic.

3. Destruction of Cyanides

The standard techniques for oxidation of cyanide such as alkaline chlorination (see report on Oxidation) have disadvantages in that they introduce other potentially toxic materials into the waste stream. Miller and Kuhn (Ref. 8) have demonstrated that a mixture of nitrite and cyanide at low pH, can be converted into cyanate, carbonate, and nitrogen gas using an activated carbon catalyst. Other workers (Refs. 9, 10) have also demonstrated that the use of granular carbon to catalyze the oxidation of cyanide to cyanate with molecular oxygen. The important variables in the process appear to be oxygen concentration and contact time. Work by Bernardin (Ref. 11) has demonstrated that the addition of other catalyst materials, particularly copper, to the activated carbon increases the rate of cyanide oxidation. The copper is present in the form of cupric ions which result in the formation of copper cyanides, which have a greater absorption capacity than copper cyanide alone. Copper may be impregnated onto the carbon or fed continuously to the bed on a one-to-one weight basis with the cyanide. During continuous feeding of copper, reaction products form precipitates of copper carbonate which can block the carbon bed. Maximum efficiency is obtained at pH 6.5 to 8.0. Activated carbon has a capacity for cyanide absorption in the range of 2-3 mg/gm of carbon. The presence of copper increases the adsorption capacity of carbon by a factor of 10. Under normal atmospheric conditions the oxygen in solution oxidizes the adsorbed cyanides and the adsorption sites are regenerated. It was determined that the copper compound precipitates which appeared after extended operation, could be removed by dissolution in acid with the recovery of the copper and the acid treated carbon neutralized and returned to service.

Cadmium, iron, zinc, and nickel have also been tested as potential catalysts, but none was as efficient as copper. It was also found that these metals inhibited cyanide removal in the presence of copper. For example, with 50 mg/ℓ of cadmium, there was practically complete inhibition of cyanide removal. Iron and zinc also inhibited the cyanide destruction, but to a smaller extent.

Tests on a number of metal plating wastes showed that the cyanide content could be reduced from about 30 ppm down to less than 0.1 mg/ℓ. Variability in the results tended to correlate with the presence of other metals in the waste streams which had an inhibitory effect on the cyanide removal efficiency. In particular, iron (and iron cyanide complexes) can cause serious fluctuation in the effluent quality.

The process has been shown to work on copper, zinc, and cadmium wastes and on coke plant wastes when pretreatment is used, such as removal of oils and tars which foul the carbon surface and removal or prevention of excess iron contamination which forms oxidation resistance complexes.

A related project sponsored by EPA (Ref. 12) is now under way at ITT Research Institute. Experiments are being carried out to study the oxidation of cyanide in a biological treatment process using activated sludge from a petroleum refinery. Small-scale experiments (at the rate of 20 liters/day) by adding the powder carbon batch-wise into the aeration section of an activated sludge system concurrently with continuous cupric chloride addition. The residence time in the system is 12 hours using a 15-day-old sludge. Lab work with a solution containing 0.5 mg/ℓ total cyanide (including complex cyanides such as ferri- and ferro-cyanide), 250 mg/ℓ of carbon and 0.5 mg/ℓ of copper, gave an effluent with a cyanide concentration of 0.02 mg/ℓ. Increasing the copper concentration by a factor of 2 reduces cyanide to less than 0.01 mg/ℓ. In further experiments using actual refinery waste effluent, ITT Research Institute has found that the organic component in the effluent competes with the cyanide for adsorption on the carbon necessitating an increase in carbon concentration to about 1,000 mg/ℓ. Under these conditions, inlet cyanide concentrations of 0.5 mg/ℓ are reduced to 0.05 mg/ℓ.

4. Oxidation of Sulfides

Wastes containing sodium sulfide, which has a very high immediate oxygen demand, can be oxidized at room temperature by bubbling air through the system. Iron and copper catalysts have been reported to catalyze the oxidation reaction (Ref. 13). The oxidation of sulfide to sulfate increases the acidity of the waste and, therefore, subsequent neutralization is required.

Spent caustic streams are an important fraction of refinery waste streams which contain high concentrations of sulfide ion. Oxidation of the sulfide to thiosulfate or sulfate is a well known process (Ref. 14). Use of cupric chloride as a catalyst (Refs. 15, 16) at 10 ppm concentration (125°C/72 psia) increased the reaction rate and gave essentially complete conversion of 2000 ppm sulfide to sulfate. High concentration of phenols which are often present in this type of effluent interfere with the oxidation.

A process developed by Duffy (Ref. 17) involves removal of oil and dissolved sulfides from oil production wastewaters prior to disposal by the injection of controlled amounts of air and soluble nickel catalysts. The mixture is pumped under pressure into a flotation cell or tank where the pressure is released and the air effects oil separation and oxidation of the dissolved hydrogen sulfide simultaneously. The nickel catalyst may be any water-soluble nickel compound, such as nickel sulfate, nickel acetate, nickel chloride, nickel sulfamate, nickel nitrate, chelated nickel, etc. Nickel concentration (0.1 – 1.0 ppm) is limited by the discoloration of the water due to the formation of black nickel sulfide. Air is added to the waste stream under a pressure of 20-50 psig to increase its solubility in water, and when the pressure is let down in the flotation cell more air is released. To improve the flotation process, catalysts should preferably be added during aeration to avoid absorption by the oil. Otherwise sulfide removal would be significantly reduced.

With temperatures of 10-65°C in the flotation cell, reaction time is about two minutes.

5. Other Applications

Laboratory work supported by the EPA at Southern Illinois University (Ref. 18) has shown that aqueous solutions of phenol and orthochloronitrobenzine (OCNB) can be catalytically oxidized at room temperature in the presence of Raney nickel catalysts and ultrasonic vibrations. Both ozone and air were studied as oxidizing agents. A Raney nickel catalyst in the presence of ozone and ultrasound reduced 500 mg/ℓ phenol to 25 mg/ℓ in three hours. Concurrent measurements of COD removal showed that phenol is first oxidized to intermediate compounds. However, 80% COD removal was obtained after 7 hours. The ozone and ultrasound alone in the absence of catalysts gave only about 40% COD removal. Experiments with OCNB and Raney nickel catalysts also initially gave intermediate breakdown products, but after 24 hours the OCNB and intermediates could no longer be detected.

Oxidation of phenolic wastes using hydrogen peroxide and ferrous salts has been investigated in the laboratory (Ref. 19). Solutions were reacted at room temperature and pH 3 with air agitation. Reaction with phenol was complete in fifteen minutes. Alkyl substituted phenols reacted more slowly, but other substituted phenols, e.g., chlorophenols reacted more rapidly. This treatment avoids the chlorinated phenols which are produced by chlorine oxidation of phenol but has the disadvantage that other oxidizable components in the waste consume additional hydrogen peroxide. Cyanides also complex the ferrous ion catalyst inhibiting the oxidation.

Cobalt hydroxide was found by Londhe and Kamath (Ref. 20) to be a very effective catalyst for the catalytic decomposition of waste sodium hypochlorite solutions to sodium chloride. The rate of reaction appeared to be higher with a cobalt hydroxide precipitate than with massive forms such as sheet or granules. Ninety percent reduction of the hypochlorite was obtained over a period of 30 hours with a cobalt concentration of 200 mg/ℓ at room temperature. At 50-55°C, over 90% decomposition was obtained in 7 to 8 hours. The catalyst did not appear to be deactivated and could be used repeatedly. Other catalysts such as copper, nickel, iron, and manganese were also tried but did not appear to be more effective than cobalt.

Catalytic oxidation with air has been tried on aqueous wastes. Laboratory studies have shown that dilute aqueous organic waste can be effectively oxidized in the vaporized stream at temperatures of 500-600°C using a copper chromate catalyst (Ref. 21). Metals, e.g. ferrous ion, can be oxidized to insoluble hydroxides at room temperature (Ref. 22) and then removed by sedimentation.

An interesting catalytic process (Ref. 23) has been reported for the recovery of fumaric acid. The waste stream is a by-product of the oxidation of ortho xylene and also contains about 30% maleic acid, together with other carboxylic acids. The solution is contacted with a 25% solution of hydrogen chloride for 2 hours at 60°C. The acid catalyzes the isomerization of maleic acid into fumaric acid which is much less soluble in water. Fumaric acid is reusable after some further purification. Sulfuric acid will also act as a catalyst.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Many catalytic processes operate at or near room temperature, thus energy requirements are minimal. For those applications which require higher temperatures, the energy requirements are the heat required to maintain the process stream at the operating temperature. In some applications, e.g., catalytic oxidation, the reaction is exothermic thus supplying some of the heat energy required.

By definition, for an equivalent rate of reaction, catalytic processes operate at a much lower temperature than the equivalent non-catalytic process, thereby resulting in lower energy consumption.

B. ENVIRONMENTAL IMPACTS

A catalytic process produces air and water emissions which are the same as those produced by the equivalent non-catalytic process. One possible exception is small losses of catalyst from liquid phase reactions where the catalyst is in solution or in the form of a slurry. In general, these losses can be made extremely small compared to other emissions from the process. If necessary, catalysts in solution can be recovered by techniques applicable to the treatment of metals. A heterogeneous catalyst system leaves a catalyst which must eventually be disposed of in some manner. This catalyst material is generally relatively inert, and in many cases can be recovered for reuse.

C. ECONOMIC ANALYSIS

Catalyst costs are a small part of process operating costs and therefore, do not have much direct impact on the economics. However, the reduced severity of operation (lower temperatures and/or pressures) which will lower fuel costs invariably causes the economics of the catalytic process to be more attractive. In some cases, the catalytic process may show higher capital costs than the non-catalytic process.

The flowsheet shown in Figure 1 depicts a process outline for the catalytic oxidation of sulfide containing wastes using a nickel catalyst. A cost breakdown for this process is shown in Table 2. Capital investment is modest; variable and fixed costs are about equal. The unit cost for sulfide oxidation is $2.75/1000 gal (0.33¢/lb sulfide).

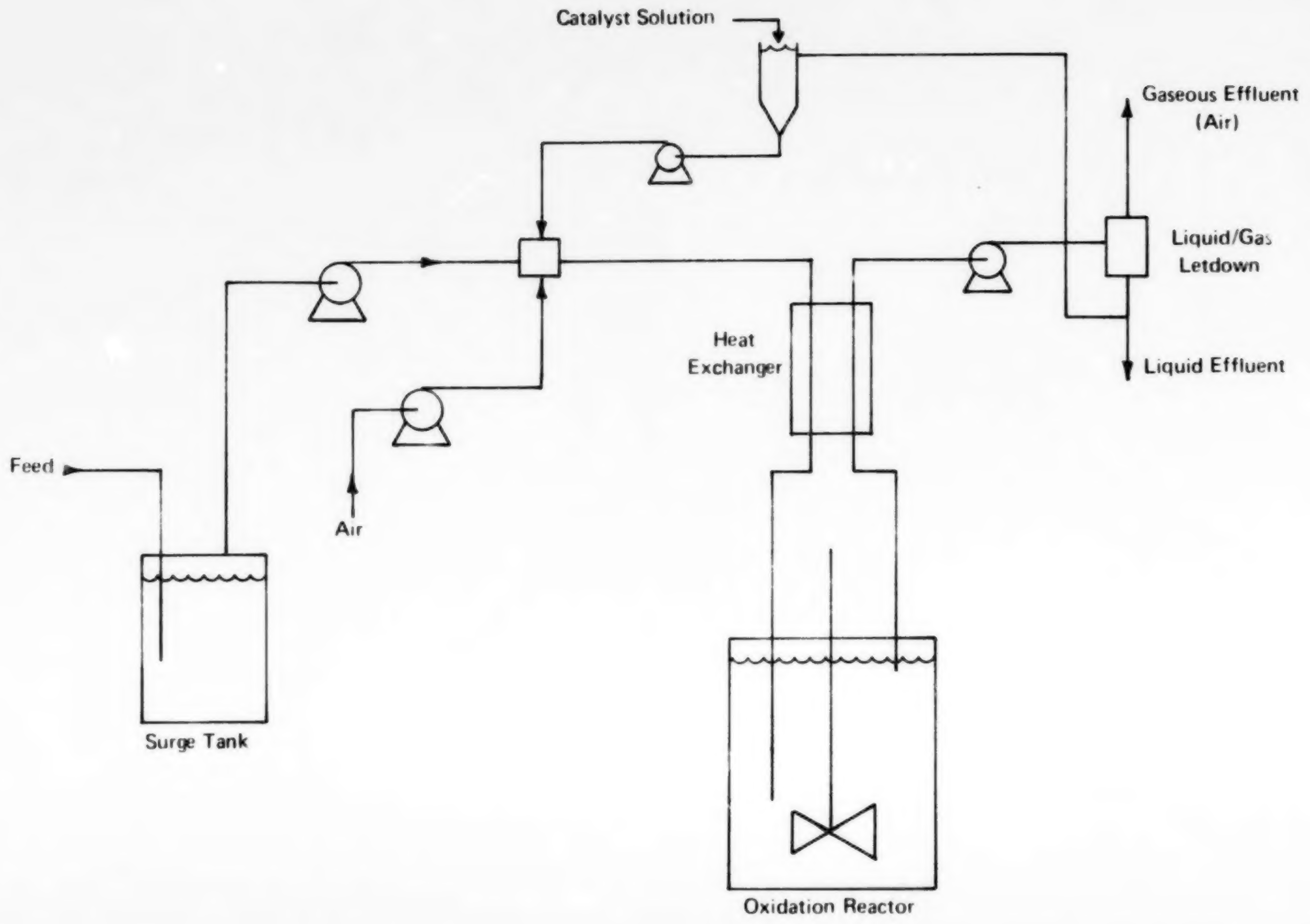

FIGURE 1 PROCESS FLOWSHEET FOR CATALYTIC OXIDATION OF SULFIDES

TABLE 2

ESTIMATED COSTS FOR CATALYTIC OXIDATION OF SULFIDES

Estimated Operating Costs for Catalysis
Basis: 100 GPM of Feed Containing 10,000 ppm Sulfide 350 Days/Year
Capital Investment: $380,000

Variable Costs	**Annual Quantity**	**Cost Per Unit Quantity**	**Annual Cost ($)**
Operating Labor	2,500 hr	$12.00/hr	$30,000
Maintenance (3% of inv./yr)			11,500
Chemical Nickel Chloride	600 lbs	$1.15/lb	700
Utilities			
Electricity	555 x 10 kWh	$0.02/kWh	11,100
Steam	4200 x 10^3 lbs	$4.00/$10^3$ lb	16,800
Total Variable Costs			$70,100
Fixed Costs			
Taxes and Insurance (2% of Inv.)			7,600
Capital Recovery (10 yr @ 10%)			61,300
Total Fixed Costs			$68,900
Total Costs			$139,000
Unit Cost ($/$10^3$ gallons)			$2.75
Unit Cost (¢/lb sulfide)			0.33

Source:

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Catalysis has a definite place in industrial waste treatment. Whenever a chemical transformation process is considered for a waste stream, the application of catalysts should also be considered to improve the operating characteristics or economics.

Work presently under way has identified several potential applications of catalysis to waste treatment, but an extended program is necessary to demonstrate their commercial practicality. Catalysts are generally quite selective and may be advantageous for the detoxification or destruction of a given component in a complex waste stream.

Areas where further exploratory work would be useful include selective detoxification by hydrogenation (similar to the dechlorination of pesticides) and low temperature air oxidation of aqueous waste streams.

A potential disadvantage is catalyst deactivation by other components in the waste stream. The extent of this problem can usually be evaluated experimentally.

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CENTRIFUGATION

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

Centrifugation is one of several well-developed liquid/solid separation processes currently being used in a variety of full-scale material processing and waste treatment applications. For the treatment of hazardous wastes, centrifugation can be used to greatest advantage in performing the function of increasing the solids concentration, and thereby reducing the volume of a high concentration liquid/solid mixture (sludge) by effecting a partial separation of the liquid and solid phases (this application is commonly referred to as "sludge dewatering").

Typically, centrifugation is capable of processing a dilute sludge (2-5% solids) into a more concentrated or "dewatered" sludge with a solids concentration ranging from 15% to 50% solids, depending on the specific material.

Centrifugation is generally technically and economically competitive with other sludge dewatering processes (such as vacuum filtration or the use of filter presses). The final selection of a dewatering process is highly dependent on the material processed and the specific requirements of the application. Often, centrifugation has an advantage over other dewatering processes in that it is more capable of dewatering sticky, gelatinous sludges.

II. PROCESS DESCRIPTION

Centrifugation is a physical process whereby the components of a fluid mixture are separated mechanically by the application of centrifugal force, which is applied by rapidly rotating the mass of fluid within the confines of a rigid vessel. Centrifugal forces acting on the revolving mass of fluid radiate outward from the center of rotation and would pull the mass of fluid apart if it were not contained within the vessel.

The centrifugal force caused by the rotation is the main driving force which effects the separation. As discussed in the companion report on precipitation, flocculation, and sedimentation, there are many forces acting on particles suspended within a fluid. These include gravitational, inertial, electrostatic, and interionic forces. If a particle is suspended within a fluid and the forces acting on that particle are in equilibrium, the particle will remain suspended. If an external force is now applied to the particle, the particle will tend to migrate in the direction of that force (provided, of course, that there is a relative difference in density between the particle and the fluid). In the case of centrifugation, if a particle is more dense than the fluid, it will tend to migrate in the direction of the centrifugal force, i.e., toward the periphery of the rotating vessel containing the fluid. If the particle is less dense than the fluid, there will be a tendency for the particle to remain near the center of rotation and the fluid to migrate toward the periphery of the vessel. Either way, particles that were uniformly dispersed throughout the fluid prior to centrifugation would now be concentrated in a specific region of the centrifuge where they can be removed as a more concentrated mixture. In centrifugation, the centrifugal force is analogous to gravitational force in the sedimentation process. In centrifugation, however, forces equal to several thousand times the force of gravity are often generated.

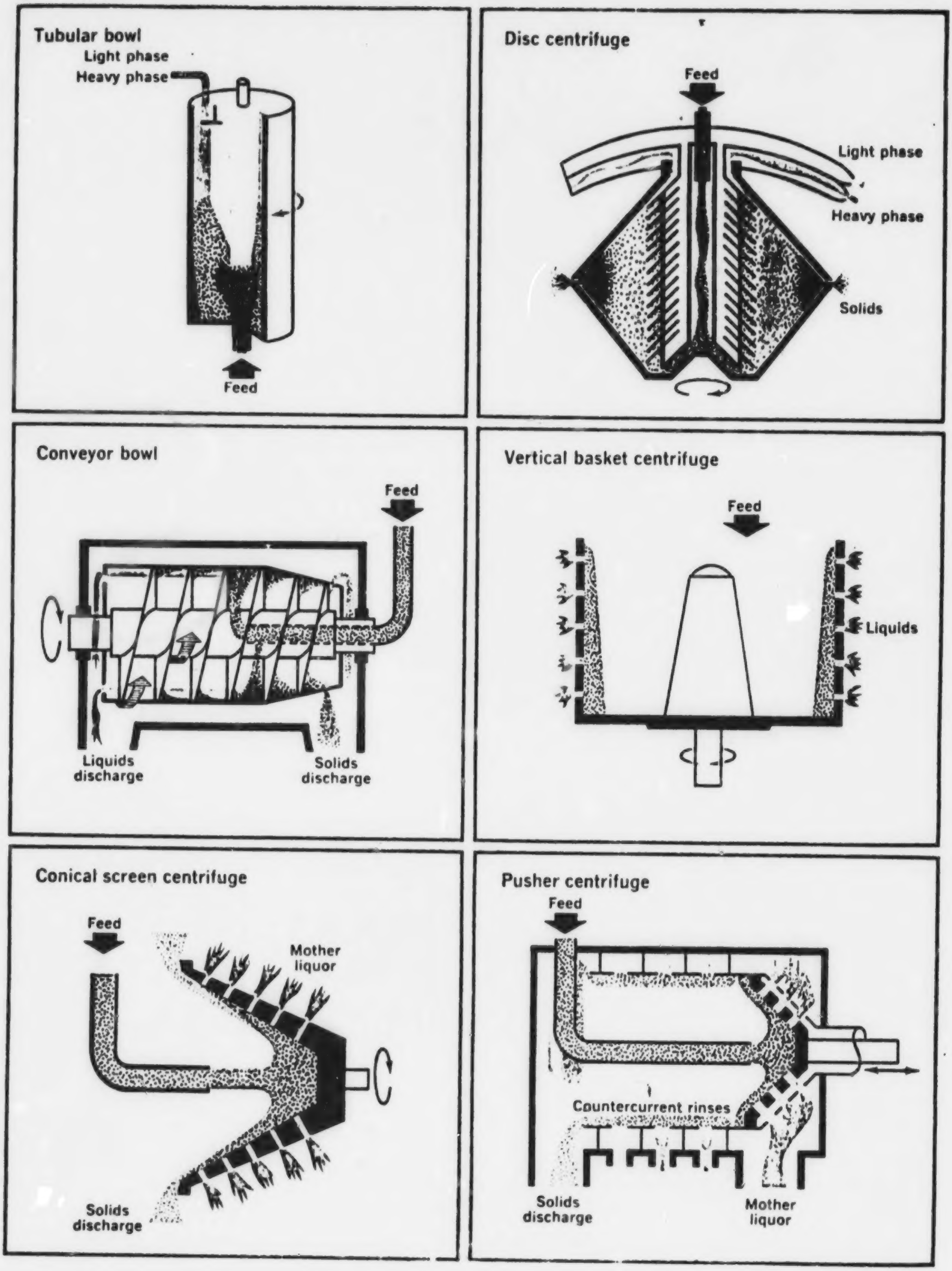
Centrifuges are in widespread use throughout industry for a variety of process and waste treatment applications. The many different applications have resulted in a large number of equipment configurations. Fundamentally, centrifuges fall into two categories:

- sedimentation centrifuges
- filtering centrifuges

In the sedimentation centrifuge the solids accumulate in a layer or "cake" on the inner wall of the rotating vessel.

In the filtering centrifuge a cake of granular solids is deposited on a filter medium held in a rotating basket.

Some of the more representative types of centrifuges are described below (Ref. 1) and are shown in Figure 1.



Tubular bowl

Disc centrifuge

Conveyor bowl

Vertical basket centrifuge

Conical screen centrifuge

Pusher centrifuge

Source: Ref. 1.

FIGURE 1 REPRESENTATIVE TYPES OF CENTRIFUGES

Tubular Centrifuge – In the tubular centrifuge, a sedimentation type centrifuge, the fluid enters the bottom through a stationary nozzle. The fluid is then accelerated to the speed of the revolving tubular bowl. Solids contained within the fluid migrate to the periphery of the bowl and form a layer on the inner wall of the bowl. The separated fluids are usually continuously displaced by the incoming feed.

Disc Centrifuge – The disc centrifuge, a sedimentation type centrifuge, consists of a revolving bowl which contains a series of conical-shaped discs that divide the feed into layers, usually not more than 0.05 inch thick. This "thin strata distribution" increases the rate of solids separation.

There are several variations of this type of centrifuge. In the "nozzle bowl" type, solids are continuously discharged through nozzles built into the bowl wall. In the "self cleaning" type, the bowl's bottom section slides downward for a fraction of a second to discharge the solids.

Conveyor Bowl Centrifuge – Also a sedimentation type centrifuge, the conveyor bowl centrifuge employs a rotating screw contained within the rotating centrifuge bowl. The screw rotates in the same direction as the bowl in which it is contained, but at a slightly lower speed. Solid particles accumulated on the inner wall of the bowl are directed by the rotating screw to the discharge point. The liquid is discharged from the other end of the centrifuge through adjustable ports.

Conveyor bowl centrifuges are available in a number of configurations. The axis of rotation can be either horizontal or vertical and the bowl may be either cylindrical or conical. The bowl configuration affects the clarity of the outlet liquid and the dryness of the cake.

Batch Centrifuge – The batch centrifuge is the most simple type of filtering centrifuge. It generally consists of a perforated metal basket that rotates about a vertical axis. Liquid flung against the inner wall of the basket is forced through the perforations by the centrifugal force, while the solids are retained and accumulate in a layer on the inner wall. After a sufficiently thick layer has accumulated, the machine is stopped, the solids removed, and the basket washed and spun dry. Although a batch machine, it is often automated so that little labor is required for its operation.

Conical Basket Centrifuge – In this variation of the filtering centrifuge, a conical screen is rotated about a horizontal axis. As in the batch centrifuge, solids are retained on the rotating screen while the liquid passes through. Due to its geometry, the conical basket centrifuge is a continuous machine. The force of the incoming feed, along with the force vector along the direction of the cone, causes the accumulated solids to be pushed out the wide end of the cone.

Pusher Centrifuges – The pusher centrifuge is a filtering basket type centrifuge, as described above, which employs an oscillating piston that travels the length of the bowl and displaces solids from the basket. It operates in a continuous mode as in the case of the conical basket type, but also has the capability of washing the coke in a *continuous* mode.

While there are many more variations, under a large number of trade names, the general types of centrifuges described above embody the basic elements of most centrifugation equipment. As mentioned, the centrifuge configuration greatly determines the type of fluid and particles that can be successfully separated. To provide perspective on the type of particles that can be separated by centrifugation and the nature of the resulting cake, a summary of general applicability, available equipment capacity, etc. (Ref. 2), is given in Table 1.

TABLE 1

APPLICATION RANGE OF CENTRIFUGES

A. SEDIMENTATION TYPE CENTRIFUGES

Characteristic	Tubular	Disc (nozzle type)	Conveyor Bowl
Minimum particle size (microns)	0.1	0.25	2
Maximum particle size (microns)	200	50	5,000
Allowable concentration of feed solids (%)	< 0.1	2-20	2-60
Condition of cake	Pasty, firm	Fluid	Firm, pasty
Typical solids handling rate (lb/hr)	0.1-5	10-3000	100-100,000
Typical liquid rate (gpm)	0.25-20	1-800	1-500

B. FILTERING TYPE CENTRIFUGES

Characteristic	Batch (vertical)	Conical Basket	Pusher
Minimum particle size (microns)	10	250	40
Maximum particle size (microns)	1,000	10,000	5,000
Allowable concentration of feed solid (%)	2-10	40-80	15-75
Condition of cake	Pasty	Relatively dry	Relatively dry
Typical solids handling rate tons/hour	0.1-1.0	5-40	0.5-50

As can be seen from Table 1, the tubular type centrifuge, while capable of removing very small particles is generally small in physical size and small in throughput. (A special variation of the tubular centrifuge is so-called ultracentrifugation in which very high forces are developed and very small particles can be separated, e.g., viruses and protein molecules. These are usually small, highly specialized, and very expensive pieces of equipment.)

The disc and conveyor bowl centrifuges, while not having as good a particle removal ability, have a much higher throughput and can handle relatively large volumes of material. Most waste treatment applications of centrifuges involve either the disc or conveyor bowl centrifuge. The various filtering centrifuges generally cannot handle very fine particles. They are, however, quite good at producing a dry cake and can handle a high solids concentration liquid that contains large size particles (such as crystals or granular material).

III. APPLICATIONS TO DATE

A. INDUSTRIAL PROCESS APPLICATIONS

Centrifugation is widely used throughout industry for a variety of liquid solid separation applications. Listed below are some common applications of the various types of centrifuges (Ref. 3).

1. Tubular Centrifuges

- Separation of oil and water mixtures.
- Clarification of viscous gums and resins such as molten chicle and nitrocellulose dope.
- Classification and removal of oversize particles and unground pigment from lacquers, enamels and dye paste.
- Clarification of essential oils, extracts, and food products such as homogenized milk and fruit juices.
- Separation of microorganisms from fermentation broths.
- Recovery of finely divided metal particles such as silver from film scrap and platinum from spent catalyst.

2. Disc Centrifuges

- Separation of wash water from fats and oils as in the process of refining vegetable oil and purifying fish and whale oil.
- Separation of acid sludges from the acid treatment of petroleum stocks.
- Concentration of dispersions such as natural and synthetic rubber latex.
- Clarification of wet process phosphoric acid.
- Separation of solvent extract from antibiotic broths.

3. Conveyor Bowl Centrifuge

- Recovery and dewatering of various crystalline solids such as salt from brine and various potash operations.
- Separation of oil and water.

- Dewatering of waste sludges.
- Recovery of powdered metal catalyst from organic reactions.
- Classification of dispersed clay.
- Recovery and dewatering of polymers such as PVC and polyolefins.
- Removal of meat tissue from animal fats.

4. Filtering Centrifuges

- Dewatering of fibrous solids such as paper pulp and chemical fibers.
- Dewatering and removal of starch from potato fibers.
- Dewatering of suspensions of medium- to -coarse crystals.
- Removal of pulp skins and seeds from various fruit and vegetable products, such as tomato juice, citrus juices, and fruit purees.
- Deoiling of metal chips.

In general, there are few industrial applications in which centrifugation is the only separation process applicable. Very often centrifugation is interchangeable with some form of sedimentation and/or filtration. The specifics of an actual application deem which separation technique is most feasible. Due to its totally enclosed operation, centrifugation is particularly well suited to treating liquids that are volatile, flammable, or otherwise pose health and/or safety hazards to operating personnel.

B. WASTE TREATMENT APPLICATIONS

The major application of centrifugation to the treatment of wastes (both hazardous and non-hazardous) is the dewatering of waste sludges generated by water pollution control systems. Centrifuges have for many years been used for the dewatering of biological sludges from municipal wastewater treatment plants and from pulp and paper mill wastewater treatment plants (Refs. 4-7). In recent years centrifugation has increased in popularity as a dewatering device and some expect it to replace vacuum filtration as the most common dewatering device (Ref. 8).

Sludges that are sticky or gelatinous are sometimes more easy to dewater by centrifugation than by vacuum filtration (although the advantage of centrifugation in practice may be hard to predict, so that comparative testing must usually be performed to determine the most effective process). Practically all of the metal hydroxide and metal sulfide sludges generated as the result of removal of soluble metals from wastewater by precipitation can potentially be dewatered by centrifugation. In such applications it is reasonable to expect that centrifugation would be capable of producing a sludge of 15-20% solids concentration. However, most precipitates of this nature are settled in a pond and removed periodically afterwards.

Some of the more exemplary waste treatment applications are summarized below (Ref. 10).

- Centrifugation can be used effectively to dewater sludges from wet scrubbers used in the steel industry for the control of basic oxygen furnace air emissions. Such sludges are composed of very fine particles.
- Centrifugation is used in the petroleum refining industry for the dewatering of oil/water separator bottoms.
- Centrifugation is used in nuclear power plants to dewater radioactive waste powdered ion exchange resins and filter precoat materials.
- Centrifugation can be used effectively to dewater calcium sulfite/sulfate sludges generated from sulfur dioxide air pollution control systems.
- Centrifugation is being used in an ethylenediamine plant to remove sodium sulfate waste crystals from toxic EDA liquor prior to discharge.
- Centrifugation is being used at an acrylonitrile plant to remove solids from acrylonitrile wastewater. The completely enclosed design facilitates confining hazardous mist and vapors. The dewatered solids are discharged to a sealed receptacle.

C. POTENTIAL APPLICATIONS

Whenever it is necessary to separate solid particles from a liquid stream or to separate two immiscible liquids from each other, centrifugation is a potential application. While centrifugation is a liquid/solid separation process in much the same sense as sedimentation, its most common function is to separate liquid from solids thereby producing a dewatered solid residue, or sludge. Because of its process characteristics and physical features, it is seldom ever used to separate solids from a liquid with the sole intent of producing a clarified liquid suitable for discharge into a receiving stream. As a full-scale waste treatment process, it is simply incapable of effecting that high a degree of solids separation. The "clarified" liquid from most industrial centrifuges will typically contain several hundred to several thousand mg/l of suspended solids, a concentration far too high to be discharged directly. (While special "ultra-centrifugation" devices can remove colloidal particles from liquids, the large scale commercially available centrifuges are not generally capable of removing truly colloidal particles.) For this reason, the most likely potential waste treatment application for centrifugation is confined to the dewatering of waste sludges.

Potential applications of centrifugation to various forms of hazardous wastes are discussed below:

Aqueous — Centrifugation is potentially applicable in the removal of solid particles from aqueous waste streams. Generally, the smaller the size of the waste stream and the higher the concentration of suspended particles, the greater will be the potential applicability. For large volume wastewater streams (over 1 million gpd) sedimentation and/or filtration is usually more technically and economically feasible.

Non-Aqueous Liquid — Centrifugation is potentially applicable to non-aqueous liquids provided that they are reasonably free flowing and are not overly adhesive. Due to its enclosed construction, centrifugation is probably more capable of treating volatile non-aqueous liquids than sedimentation or filtration.

Slurries and Sludges — As previously discussed, centrifugation is currently being used for the dewatering of slurries and sludges; and in fact, this is the major waste treatment application of centrifugation. Being a physical process, centrifugation cannot alter the nature of any hazardous constituents in the sludge; it can only reduce the volume of the sludge and thereby somewhat alleviate the ultimate disposal problem.

Tars — Provided that the tar is not overly viscous (as most are) it is conceivable that centrifugation could be used to remove solid particles suspended within the tar. This is not one of the more promising applications of centrifugation.

Solids, Dry Powders — Due to the fundamental requirement that the waste material be in a fluid state, centrifugation is definitely not applicable to the treatment of solids or dry powders.

Gas — Cyclonic devices, which are based on centrifugation, have been used for many years to remove particulate matter from gas streams. While these devices are based on centrifugation, they are usually considered separately and are not referred to as centrifuges.

Table 2 summarizes the potential applicability of centrifugation to the treatment of various forms of hazardous wastes.

TABLE 2

POTENTIAL APPLICABILITY OF CENTRIFUGATION TO VARIOUS FORMS OF HAZARDOUS WASTES

Waste Form	**Potential Applicability**
Aqueous (dilute, ≤ 2% solids concentration)	Low
Non-Aqueous Liquid	High
Slurries	High
Sludges	High
Tars	Low
Solids	Not Applicable
Dry Powders	Not Applicable
Gases	High (cyclonic devices only)

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Centrifuges require electrical power to rotate the fluid-containing vessel in which the centrifugal force is applied. Power requirements generally range from 0.3-1.2 horsepower per gal per minute of inlet liquid.

Compared to energy-intensive processes such as incineration or distillation, centrifugation has a low energy requirement. In most cases, the energy requirements of centrifugation are equal to or slightly greater than those of vacuum filtration or press filtration, both of which are commonly used for sludge dewatering. In general, energy consumption is usually not a major factor in the selection of a sludge dewatering process.

B. ENVIRONMENTAL IMPACTS

The intended product of centrifugation is a liquid-solid mixture (dewatered sludge) of a significantly higher solids concentration than the liquid-solid mixture prior to centrifugation (wet sludge). Since there is not a complete separation of the liquid and solid phases, it is inherent in the fundamental principle of centrifugation that the final product will contain a certain fraction of the original liquid. If this liquid originally contained soluble hazardous components, then the dewatered sludge will also be contaminated with the same substances. While centrifugation can alleviate land disposal problems by concentrating the waste into a smaller volume, it has little potential for actually decontaminating a waste stream.

The clarified liquid, or concentrate, due to the fact that it typically contains a high suspended solids concentration (several hundred to several thousand mg/l) can very rarely be discharged into a waterway without some form of treatment. This feature is seldom a serious problem, because the typical practice is to return this liquid stream to the clarifier from which the sludge originated.

As a rule, there are no inherent air emissions from centrifugation. Due to almost totally enclosed construction, potential air emissions from the processing of volatile materials are minimal in centrifugation. (It is for this reason that centrifugation is usually selected for dewatering truly dangerous materials, such as radioactive wastes.)

C. ECONOMIC ANALYSIS

Since centrifugation has been in full-scale use for many years the operating parameters and economics are well defined and well documented.

The capital cost of a centrifuge of a particular type is mainly a function of its rated horsepower. The required power, in turn, is a function of the volumetric throughput, i.e., gallons per minute of liquid fed to the centrifuge and the required rotational speed of the centrifuge. The rate at which a liquid can be fed to a centrifuge depends on the type of centrifuge, feed solids concentration, desired solids removal efficiency, liquid viscosity, and particle size and density. The allowable feed rate varies considerably from application to application. For the dewatering of most waste sludges, a typical rating is 0.3-1.2 horsepower per gallon per minute throughput.

To illustrate the economics of centrifugation for sludge dewatering applications, an economic analysis has been performed on the use of centrifugation in the treatment of a specific waste stream.

The selected waste stream is a 36,000 gpd wet sludge stream containing 4% (by weight) of zinc hydroxide precipitates. This stream would be typical of a waste metal hydroxide sludge that is commonly produced in the removal of heavy metals from wastewater by precipitation, flocculation, and sedimentation.

An illustrative flow diagram of the selected treatment system is presented in Figure 2.

Referring to Figure 2, a brief description of the process scheme is as follows:

- The wet zinc hydroxide sludge (after being drawn off from the previously mentioned precipitation, flocculation, and sedimentation step) is pumped to two 12 horsepower conveyor bowl centrifuges.

- To aid in the dewatering process, synthetic polyelectrolyte is added to the sludge prior to its entering the centrifuge. The polyelectrolyte helps flocculate small sludge particles into larger particles, and thereby improves the overall solids removal efficiency of the centrifuge. Such polyelectrolytes are typically fed at a rate of 3 lbs per ton of dry solids processed.

- The centrifuge separates the 4% solids sludge into two streams: (1) the dewatered sludge containing 25% solids, and (2) the partially clarified liquid, or centrate, which contains 800 mg/liter of suspended solids.

- The dewatered sludge is collected and transported via a conveyor belt to a receiving station where it is then trucked away to landfill.

- The centrate, which still contains an appreciable amount of suspended solids, is returned to the clarifier from which the sludge was originally drawn. Via the flocculation and sedimentation processes taking place in the clarifier, the returned suspended solids eventually become part of the sludge stream once more.

Cost estimates were developed for the process scheme depicted in Figure 2 and these are presented in Table 3. The total annual cost is divided into variable costs, which include

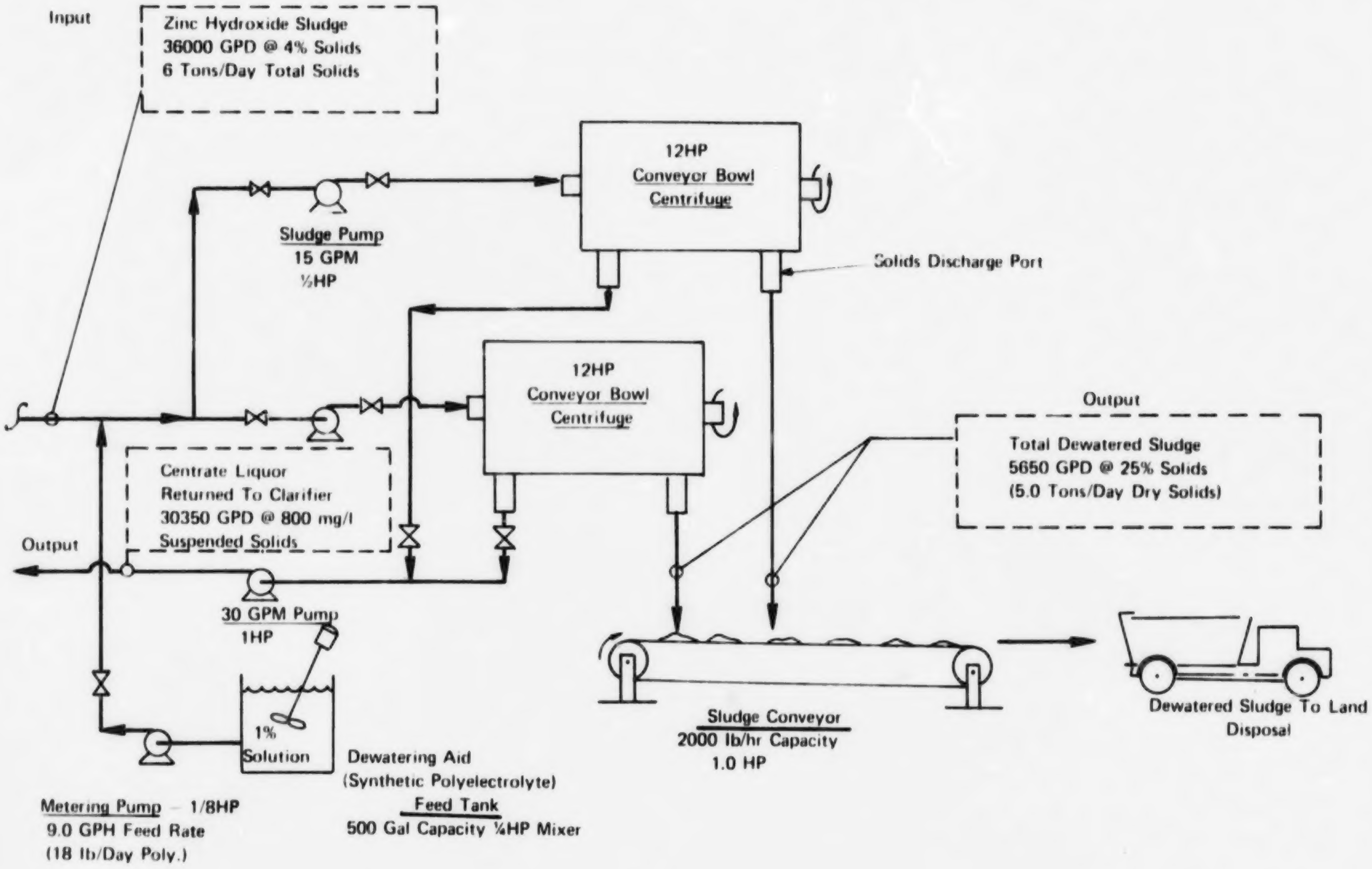


FIGURE 2 CENTRIFUGATION OF WASTE SLUDGE – ILLUSTRATIVE FLOW DIAGRAM
WASTE STREAM – ZINC HYDROXIDE SLUDGE

TABLE 3

COST ESTIMATES FOR ILLUSTRATIVE CENTRIFUGATION SYSTEM

Waste Stream: Zinc Hydroxide Sludge
36,000 gpd of 4% $Zn(OH)_2$ (by weight)
6 tons/day Zinc Hydroxide

Capital Investment – $140,000

Variable Costs	**Annual Quantity**	**Cost Per Unit Quantity**	**Annual Cost ($/yr)**
Operating Labor (including supervision plus overhead)	2,100 mh/yr	$12.00/hr	$25,200
Maintenance (labor plus materials)	–	–	5,600
Chemicals			
Polyelectrolyte dewatering aid	6,300 lb/yr	$ 2.00/lb	12,600
Electrical Energy	170,800 kWh/yr	$ 0.02/kWh	3,400
Total Variable Cost			$46,800/yr
Fixed Costs			
Capital Recovery (10 years @ 10%)	–	–	22,800
Taxes & Insurance (@ 2% of capital investment)	–	–	2,800
Total Fixed Cost	–	–	$25,600/yr
Total Annual Cost			$72,400/yr
Unit Cost (cost per ton of dry solids processed)			$34.50/ton

Notes:
1. Capital investment adjusted to January 1976 (Engineering News Record Construction Cost Index – 2305).
2. Operating costs are based on a 24-hour per day, 350 day per year operating period.
3. Costs do not include sludge hauling and landfill costs.

Source: Arthur D. Little, Inc., estimates.

all the components of the direct operating cost, and fixed costs, which include capital-related items such as capital recovery and taxes and insurance.

For the illustrative system shown, the total annual cost is $72,400/yr, which on a unit cost basis translates to $34.50 per ton of dry solids processed. Such a cost is typical for this type of treatment system.

In considering treatment economics in a general sense, it is necessary to take into account economy-of-scale effects. The capital cost of most process equipment does not vary linearly with size, but rather, as the 0.5-0.8 power of size. Thus, tripling the size of a piece of process equipment will not triple the cost but will only approximately double the cost. To illustrate this effect, two additional cost estimates were prepared, one for a treatment system one-third the size of that used in the example, and one for a system three times its size. These estimates are presented in Table 4.

TABLE 4

CENTRIFUGATION – COST ESTIMATES AS A FUNCTION OF SIZE

	Treatment System Throughput		
	12,000 gpd **2 tons/day solids**	**36,000 gpd** **6 tons/day solids**	**108,000 gpd** **18 tons/day solids**
Capital Investment	$100,000	$140,000	$245,000
Variable Costs			
Labor	19,200	25,200	39,200
Maintenance	4,000	5,600	9,800
Chemicals	4,200	12,600	37,800
Electrical Energy	1,100	3,400	10,200
Total Variable Cost	$ 28,500	$ 46,800	$ 91,000
Fixed Costs			
Capital Recovery	16,300	22,800	39,900
Taxes and Insurance	2,000	2,800	4,900
Total Fixed Cost	$ 18,300/yr	$ 25,600/yr	$ 44,800/yr
Total Annual Cost	$ 46,800/yr	$ 72,400/yr	$135,800/yr
Unit Cost (cost per ton of dry solids solids processed)	$ 66.90/ton	$ 34.50/ton	$ 21.60/ton

Notes: All costs are for the waste stream and treatment process scheme depicted in Figure 2 of this study.

Source: Arthur D. Little, Inc., estimates.

As can be seen from Table 4, over a 9-fold size range, the unit treatment cost for the illustrative treatment system varies from $66.90/ton for the small system to $21.60/ton for the large system.

The waste streams used in the economic analysis is a particularly wet and difficult sludge to dewater. In most cases centrifugation dewatering costs usually range from $20/ton to $45/ton of dry solids. Such costs are generally comparative with most of the alternative sludge dewatering methods, e.g., vacuum filtration and press filtration.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

A. GENERAL ADVANTAGES AND DISADVANTAGES

1. Advantages

- *Demonstrated Operation Practicality* – Centrifugation is in widespread full-scale use for both industrial processing and waste treatment applications.

- *Versatility* – Centrifugation is capable of effecting liquid/solid separation on a wide variety of waste sludge streams. Many types of waste sludges are amenable to dewatering by centrifugation, particularly difficult-to-dewater sludges.

- *Physically Compact* – For a given volumetric throughput, centrifugation usually requires far less space than other liquid/solid separation processes. Centrifuges are largely self-contained pieces of equipment and are usually independent of major auxiliary equipment.

- *Reasonable Cost* – Centrifugation is generally cost competitive with alternative sludge dewatering processes, i.e., vacuum filtration, and press filtration.

- *Minimal Secondary Air Pollution Effects* – As with almost all sludge dewatering processes, there are no inherent secondary air pollution effects. Centrifugation has a decided advantage over other sludge dewatering processes in that it is easily capable of totally enclosed operation – a feature of great importance when dealing with volatile and/or highly dangerous materials.

- *Low Operating Labor Requirements* –Centrifuges generally require very little operator attention.

- *Often Capable of Dewatering Difficult-to-Filter Sludges* – Sludges which are highly sticky or gelatinous are often difficult to dewater by filtration techniques, as they tend to clog verv fine filter media and tend to pass through coarser media. Metal hydroxide sludges tend to have these properties. In many cases, centrifugation is a more suitable dewatering technique for such sludges.

- *Reduced Chemical Requirements* – Very often, difficult-to-dewater sludges require the use of dewatering aids such as lime and/or ferric chloride to both break the hydrous gel structure within the sludge and to flocculate small sludge particles. While lime and/or ferric chloride are often required for the dewat of sludges via vacuum filtration, less offensive, non-corrosive organic polye trolytes are usually employed when using centrifugation.

- *Potential for Waste Recovery* – Centrifugation is a physical separation process, and, therefore, does not destroy or seriously alter any of the components of the material treated. If either the liquid phase or the solid phase of a particular waste is recoverable, and if such recovery is deemed feasible, centrifugation will not be incompatible with the overall objective of recovery.

2. Disadvantages

- *Incomplete Removal* – Commercial centrifugation equipment, while capable of effecting a desirable degree of sludge dewatering, is usually incapable of producing a high purity liquid stream or a completely dry solid stream. Both the liquid product of centrifugation (concentrate) and the dewatered sludge will each contain a certain fraction of the original liquid and solid phases. If either the original liquid or the original solid is contaminated with hazardous materials, the product of centrifugation will also be contaminated to a certain degree. This is a disadvantage inherent in all full-scale liquid/solid separation processes.

- *Non-selective* – Being a purely physical separation process, centrifugation cannot be expected to separate chemical components from each other when they are present in the same phase.

- *Relatively High Maintenance When Processing Abrasive Materials* – Over the years centrifugation has developed a reputation of being a process requiring high maintenance. Many maintenance problems experienced with centrifugation have been the result of handling abrasive materials which rapidly cause wear within the finely machined internal moving parts of the centrifuge. Lower speed operation and the use of ceramic wear plates have eliminated many of these maintenance problems, although other dewatering processes are not quite as vulnerable to abrasive materials.

- *Non-destructive* – Being a physical separation process, centrifugation is not capable of destroying or chemically altering hazardous materials. While this feature can sometimes be an advantage when recovery is possible, it is a disadvantage when recovery is not possible. This, of course, is a limitation of all physical liquid/solid separation processes.

B. CONCLUSION

Centrifugation is a well-developed process currently being used in a variety of full-scale material processing and waste sludge dewatering applications and it is anticipated that this will continue to be the case. The operational parameters and economics of centrifugation are well defined and well documented. For sludge dewatering, centrifugation is usually technically and economically competitive with other commonly used processes.

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B. ORGANIZATIONS CONTACTED

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South Walpole, Mass.

CHLORINOLYSIS

Prepared by

Joan B. Berkowitz

I. CONCLUSIONS AND RECOMMENDATIONS

- Chlorinolysis is capable of converting most liquid chlorinated hydrocarbons completely to carbon tetrachloride.
- It is not really a waste treatment process, but a manufacturing process for carbon tetrachloride that was chlorocarbon waste streams and residuals as feedstocks.
- There are sufficient suitable chlorocarbon wastes generated in the Gulf Coast region to support at least one 25,000 ton/yr chlorinolysis plant, and the economics are favorable.
- The process has excellent resource recovery potential, provided that there is a sufficient market for the CCl_4 produced.
- Legal and institutional problems that might militate against transfer of wastes from generators to an operating chlorinolysis unit should be investigated.

Chlorinolysis is not a process that will be used by any waste treatment facility. It is, however, a very promising manufacturing process that can accept a large quantity of toxic waste.

II. PROCESS DESCRIPTION

A. BACKGROUND

At temperatures around 500°C in the presence of excess chlorine, the carbon-carbon bonds of hydrocarbons can be broken and the molecular fragments can react with chlorine to form chlorinated hydrocarbons of shorter chain length. The process was termed "chlorinolysis" by E.T. McBee of Purdue University (Ref. 1). It is essentially a pyrolysis process, carried out in the presence of chlorine.

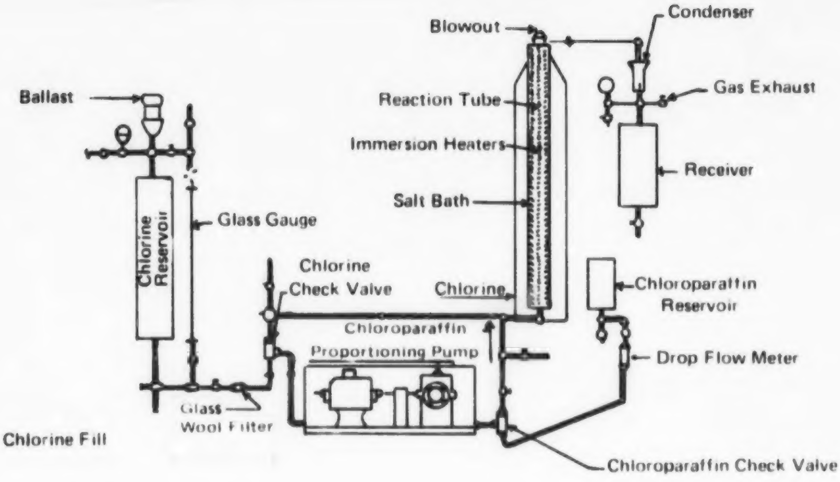
In experiments reported by McBee in 1941 (Ref. 1), mixtures of carbon tetrachloride, hexachloroethane, and hexachlorobutadiene were generated by reaction of tetrachloropentances with chlorine at temperatures of 330-500°C and pressures of 400-1000 psi. The weight percentage of each compound in the mixture varied from 10-24% for CCl_4, 35-76% for hexachloroethane, and 8-49% for hexachlorobutadiene, depending upon the temperature and pressure. At 400°C and 1000 psi, conversions to carbon tetrachloride and hexachloroethane were approximately 90%.

McBee's laboratory apparatus is shown schematically in Figure 1. The design is complicated due to the explosive nature of chlorine/hydrocarbon mixtures, and the very high reactivity of liquid chlorine at high temperatures and pressures. Before even starting work, McBee measured the explosion limits of dichloropentane/chlorine mixtures, and found that they ranged between 6 and 9 moles of chlorine per mole of dichloropentane. Thus the use of excess chlorine, mole ratio greater than 12:1, permitted reactions to occur well outside of the explosive range. The use of excess chlorine as a diluent to insure safe operation, while very well known today, was a research finding of major importance in 1941 when McBee did his pioneering work.

Recently, Hoechst-Uhde in Germany patented a chlorinolysis process (they actually use the term "chlorolysis") to manufacture carbon tetrachloride from chlorinated wastes and residues. A semicommercial plant producing 6000-8000 tons/yr of carbon tetrachloride has been in operation in Frankfurt since November 1970. A 50,000 ton/yr plant is planned for the same site.

B. UNDERLYING PRINCIPLES

The reaction of chlorine with chlorinated hydrocarbons or benzene to form carbon tetrachloride is thermodynamically and kinetically favorable at pressures above 50 atm. and temperatures above 500°C (Ref. 2). As shown by the entholpy values in Table 1, the reactions are sufficiently exothermic for the most part to permit an adiabatic mode of operation. The ratio of HCl for disposal to salable CCl_4 product varies from zero to two, compared to four in conventional production of CCl_4 by chlorination of methane. The feedstocks listed in Table 1 are typical of those found in waste streams generated in the production of



Source: Ref. 1.

FIGURE 1 LABORATORY APPARATUS FOR CHLORINOLYSIS

TABLE 1

TYPICAL CHLORINOLYSIS REACTIONS

Organic Feedstock	Process	Enthalpy, $\Delta H^\circ_{298^\circ K}$, kcal/mole	Mole ratio, HCl/CCl_4
Hexachloroethane	$CCl_3\text{-}CCl_3+Cl_2 \rightarrow 2CCl_4$	15	0
1,2-Dichloroethane	$CH_2Cl\text{-}CH_2Cl+5Cl_2 \rightarrow 2CCl_4+4HCl$	106	2
1,2-Dichlorobutane	$CH_2Cl\text{-}CHCl\text{-}CH_3+8Cl_2 \rightarrow 3CCl_4+6HCl$	142	2
Hexachlorobutadiene	$CCl_2{=}CCl\text{-}CCl{=}CCl_2+5Cl_2 \rightarrow 4CCl_4$	96	0
Benzene	$C_6H_6+15Cl_2 \rightarrow 6CCl_4+6HCl$	300	1
Hexachlorobenzene	$C_6Cl_6+9Cl_2 \rightarrow 6CCl_4$	140	0

Source: Ref. 2

vinylchloride, propylene oxide, allyl chloride, perchloroethylene, and mono- and di-chlorobenzenes. As indicated above, the reactions must be run with excess chlorine to avoid explosions. This excess chlorine also serves to regulate final temperatures to below 620°C, where corrosion and other problems develop.

C. OPERATING CHARACTERISTICS

1. Feed Streams

In principal any liquid chlorinated hydrocarbon mixture can be used as feedstock for the process. The feed streams should be free of solids. The sulfur content should not exceed 25 ppm to avoid corrosion problems.

The feed streams may contain up to 5% non-chlorinated aromatic hydrocarbons. Small quantities of oxygen containing organics may be tolerated, although the phosgene produced by chlorinolysis in this case can create serious pollution control problems.

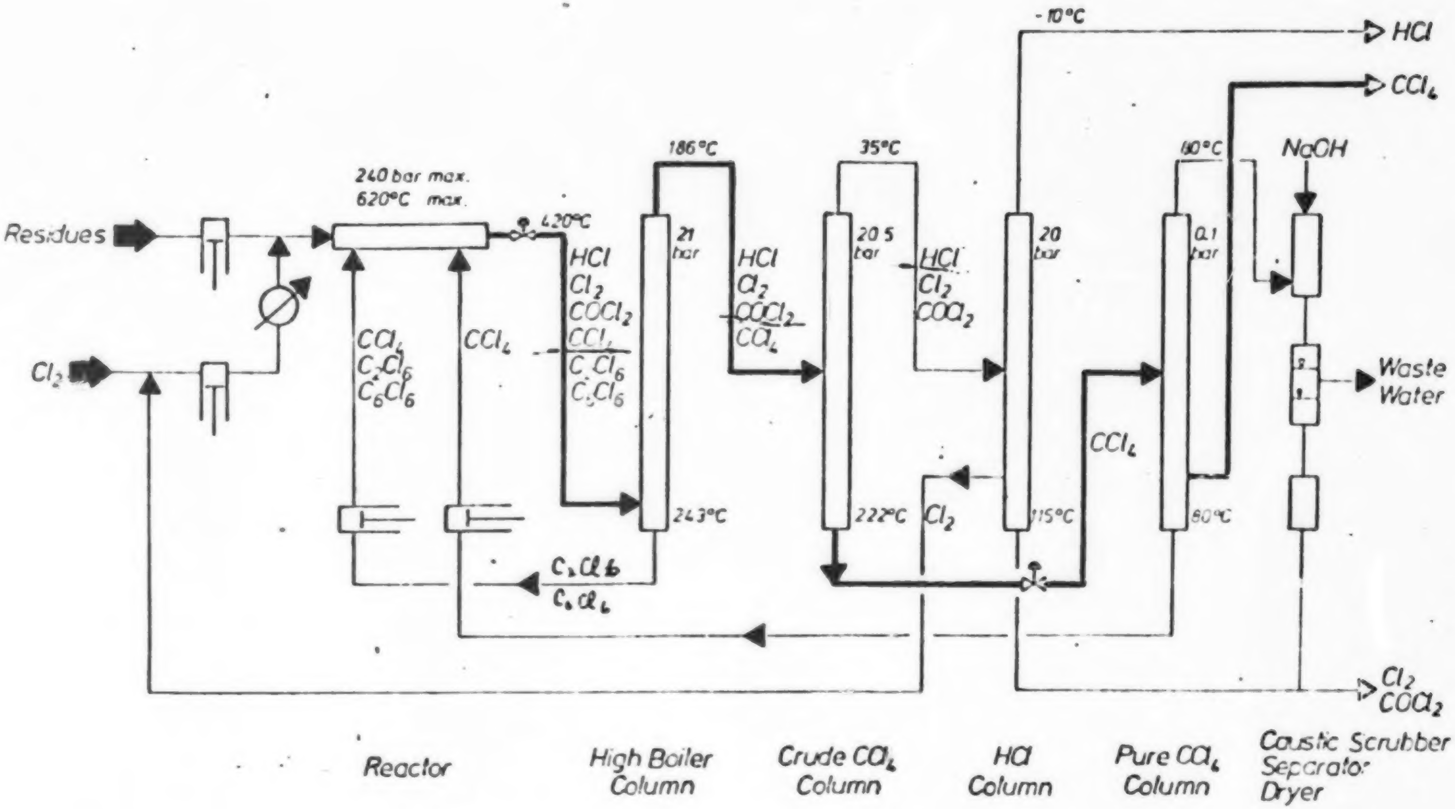
2. Mode of Operation

A schematic diagram of the Hoechst-Uhde chlorolysis process is shown in Figure 2 (Ref. 2). The organic feedstock and preheated chlorine are introduced into a very high purity seamless nickel tube reactor. Since the nickel tubing will not withstand the reaction pressure (240 atm), it is surrounded by a stainless steel jacket (Ref. 3).

Chlorine liquid is withdrawn from drums, and solids (e.g., $FeCl_3$ and HCB) are removed. The chlorine is cooled and compressed with a diaphragm pump, and passed through a preheater into the lower end of the reaction chamber. A chlorine pressure of 4 atm is needed on the suction side. Organic feed is stored at 4 atm, compressed with a diaphragm pump, and premixed with the chlorine before introduction into the reactor.

The reactor chamber is provided with electric heating. When the temperature is raised to 500°C, and the pressure adjusted to 240 atm, chloroinolysis is initiated. Since the reactions are exothermic, the electric heaters are turned off after initiation, and the reaction is allowed to proceed at 240 atm with an adiabatic end temperature of 620°C. The final temperature is regulated with chlorine, which must be at least 20% in excess and normally should be at least 50% in excess of theoretical.

At the end of the reaction, products are quenced to about 500°C with cold carbon tetrachloride bled from the output stream. The temperature is further reduced to about 420°C by releasing the pressure to 21 atm., and an air cooler is then used to bring the temperature to about 210°C. The products of reaction are generally a mixture of HCl, unreacted Cl_2, phosgene ($COCl_2$) from any oxygenated compounds present, the desired output CCl_4, and incompletely reacted hexachloroethane, C_2Cl_6, and hexachlorobenzene C_6Cl_6, which must be recycled to the process.



Source: Ref. 2.

FIGURE 2 CHLORINOLYSIS PROCESS HOECHST AG

The reaction products are separated by distillation in four columns. In the first, or High Boiler/Column, HCl, Cl_2, CCl_4 and $COCl_2$ go overhead, and C_2Cl_6 and C_6Cl_6 are recycled from the bottom of the column back to the reactor. The second or Crude CCl_4 column separates HCl, Cl_2 and $COCl_2$ as head product from CCl_4 bottoms. The crude carbon tetrachloride bottoms are purified in an atmospheric distillate column and a side stream is taken for quenching the reaction products.

The head product from the Crude CCl_4 column, consisting of HCl, Cl_2, and $COCl_2$ is separated in the HCl column. Chlorine is recycled to the reactor; HCl and phosgene might have value as by-product but would normally be passed through a caustic scrubber prior to disposal.

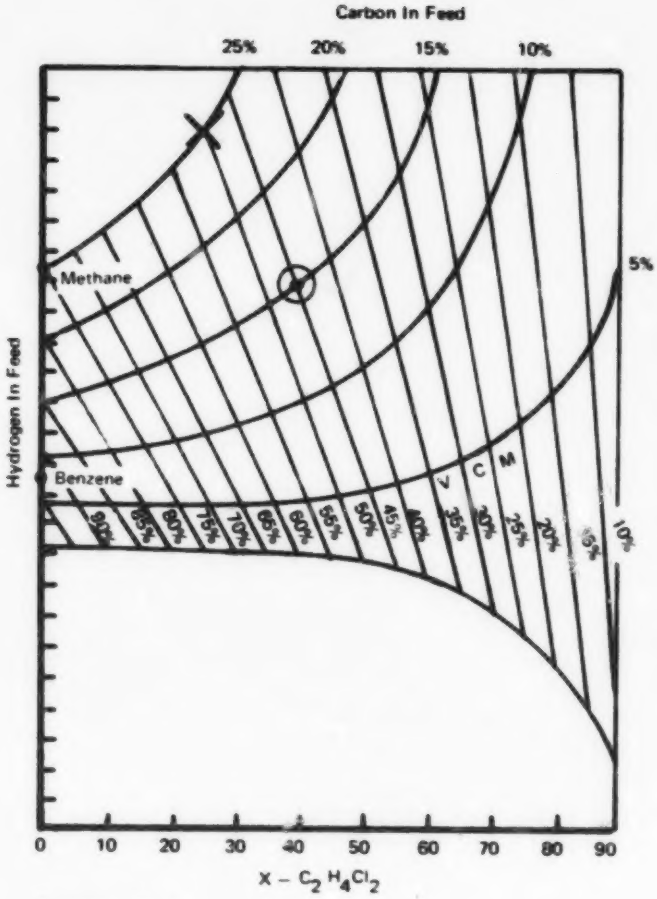
Figure 3 presents a rough estimate of the required chlorine consumption for production of 1 kg of CCl_4 from feedstocks with various Cl:H:C mole ratios. The graph is entered with the appropriate mole percentages of Cl, H, and C, and the chlorine consumption is read from the right hand scale. A typical feedstock might consist of residues from production of various chlorinated hydrocarbons. To illustrate the use of the graph, we may consider a 1,2-dichloroethane ($C_2H_4Cl_2$) feed, with 25 mole % C, 50 mole % H and 25 mole % chlorine. This composition is indicated with an X on the graph and corresponds to a chlorine consumption of 2.3 kg/kg of CCl_4 produced. The balanced reaction is:

$$CH_2Cl\text{-}CH_2Cl + 5Cl_2 \rightarrow 2CCl_4 + 4HCl$$

Thus, 5 moles of Cl_2 or 355 gram-moles, should produce 2 moles or 308 gram moles of CCl_4. The theoretical chlorine consumption per kg of CCl_4 produced is thus 1.15 kg. The figure of 2.3 read off the graph corresponds to a 100% excess chlorine. The point marked 0 corresponds to a feed composition of 15%C, 45%H and 40%Cl. Theoretically, for this composition lkg of Cl_2 would be required for each kilogram of CCl_4. The graph gives a Cl_2/CCl_4 ratio of 1.8 corresponding to an 80% excess chlorine.

3. Output Streams

The chlorinolysis process, unlike others discussed in this report, was not developed as a waste disposal process, but as a production process for CCl_4 using waste or residuals rather than virgin materials as feedstocks. The process therefore produces carbon tetrachloride at high yield as a salable product, and a waste stream consisting of HCl and phosgene. No information is given in the literature on the percentage conversion of a typical feed mixture, and therefore the quantity (if any) of unreacted chlorocarbons for disposal.



Source: Ref. 4.

FIGURE 3 CONSUMPTION OF CHLORINE FOR CCl_4 PRODUCTION USING VARIOUS FEED STOCKS

III. APPLICATIONS TO DATE

A. ALTERNATIVE ROUTES TO PRODUCTION OF CCl_4

An important commercial route since the mid-1920's for the preparation of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride in the United States has been the vapor phase thermal chlorination of methane. It is carried out on a large scale by Dow Chemical, Diamond Alkali, and Allied Chemical. It is a high temperature (350-400°C) process, but not high pressure, and can be modified by increasing the reaction temperatures to produce pechloroethylene as the major product. It is not, of course, a chlorinolysis process, since it involves no pyrolysis step.

More recently in the U.S., carbon tetrachloride has been produced by a vapor phase perchlorination process. Typical operating temperatures and pressures are 650°C (650°C) and 30-40 psi. Feedstocks are C_3 or lower hydrocarbons and chlorocarbons, and the reaction takes place in the presence of excess chlorine. It is a chlorinolysis process since C_3 feedstocks are broken down to C_1 and/or C_2 products. One manufacturer indicated that typical feedstocks include waste streams from vinyl chloride monomer manufacture, allyl chloride waste products, and virgin propylene dichloride. The process can readily be controlled to produce either carbon tetrachloride or perchloroethylene. The perchlorination process will not tolerate high concentrations of sulfur, due to the generation of a foul smelling product, unacceptable to the dry cleaning industry. The process will also not tolerate high concentrations of oxygen, due to its inhibiting effect on the pyrolytic chain reactions, believed to be an essential part of the reaction mechanism; and to its corrosive effects. Cell gas from chlorine production, for example, cannot be fed directly to the reactor. A conservative maximum is 300 ppm of O_2 in the chlorine gas and 4% in the feedstock in the form of oxygenated organics. A third process for CCl_4 production in the U.S. is chlorination of CS_2, but this process cannot be adapted to produce perchloroethylene, and Stauffer has indicated that it will shut down its plant if the demand for CCl_4 in Freon production falls off.

In Germany, methane and low molecular weight feedstocks are in very short supply, but carbon tetrachloride is an exceedingly important chemical intermediate. In the late 1960's, Hoechst in Germany developed and patented its chlorinolysis process to manufacture carbon tetrachloride from chlorinated wastes and residues derived from plants manufacturing vinyl chloride, herbicides, pesticides, solvents, etc. It is important to remember that the Hoechst process is first and foremost a manufacturing process, and only incidentially a waste disposal process. The fact that waste streams are used as feedstocks simply reflects the availability of these streams and the scarcity of virgin materials in Germany. Since 1970, Hoechst has had an 8000 metric ton/yr plant in operation in Frankfurt, and will be designing two full-scale plants for the USSR.

B. SUITABLE WASTE STREAMS

The conversion of agent Orange to carbon tetrachloride in a 100 g/hr laboratory chlorinolysis reactor was studied by Diamond Shamrock under a small EPA-Air Force Contract (Ref. 5). Agent Orange is a 50/50 mixture of n-butyl 2,4-dichloro-and 2,4,5-trichloro-phenoxyacetates. It also contains dioxin (TCDD), a powerful teratogen, as an impurity. Since all of the components are oxygenated, they are not ideally suited to chlorinolysis. Nonetheless, Orange diluted 1:1 with carbon tetrachloride, was completedly converted by chlorinolysis to CCl_4, with HCl and phosgene as by-product. The temperature was somewhat higher than in the Hoechst process (800°C vs 620°C) and the pressure was somewhat lower (300 psig vs 3400 psig). Dioxin was not detectable in the output streams, and animal tests of the output streams revealed no effects attributable to dioxin. Hoechst-Uhde of Englecliffs, NJ, the U.S. subsidiary of Hoechst, has processed several gallons of chlorinated industrial wastes for the EPA in a 10-kg/hr laboratory chlorinolysis reactor. The draft report summarizing the work has been submitted, but has not yet been released. The wastes examined included agent Orange, VCM residues perchlorothylene residues, and vinylidine chloride residues. The last two streams contained more than 80% hexachlorobutadiene. The VCM residues contained 24% 1,1,2-trichloroethane, 13% chlorobenzene and dichlorobutane, as well as other chlorinated hydrocarbons in concentrations of 1-15%. There is every reason to expect that the Hoechst Uhde tests will be successful, in view of the fact that similar waste streams, with the exception of agent Orange, have been processed in the Hoechst chlorolysis plant in Frankfurt.

In view of the fact that chlorolysis is basically a production process for carbon tetrachloride, it would only be used practically on a large scale. From data given in a recent EPA-HWMD industry study (Ref. 6), the chlorinated hydrocarbon wastes available from perchloroethylene chloromethane and epichlorohydrin manufacture alone may be estimated as over 111,000 metric tons/yr. Based on the composition of the waste streams, close to 400,000 metric tons/yr of CCl_4 could be produced if they were all converted. A large fraction of the waste-generating plants are concentrated in the Gulf Coast region. For comparison, the total U.S. production of carbon tetrachloride in 1973 was 517,000 metric tons/yr, and the typical plant size was about 50,000 metric tons/yr. Therefore, it would appear to be technically feasible to operate a chlorinolysis plant based on waste feed streams in the Gulf Coast area. The major problem is a possible overcapacity for CCl_4 production if Freon use should be curtailed.

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENERGY REQUIREMENTS

Electricity and fuel requirements per ton of CCl_4 produced are relatively small—135 kWh and 794 Btu, respectively.

B. ENVIRONMENTAL IMPACTS

The quantity of chlorocarbon wastes available is enormous, and the most acceptable method of disposal is probably incineration. This is relatively expensive, requires supplementary fuel due to the low Btu content of the wastes, and close control of the inevitable HCl emissions. Chlorinolysis offers the possibility of resource recovery. The only problem is that the future demand for the carbon tetrachloride produced is currently uncertain. A large fraction of the CCl_4, produced is used as an intermediate in fluorocarbon manufacture for aerosol propellants. Questions have been raised about the effect of fluorocarbon aerosols on the ozone layer although they have not yet been resolved. The chlorolysis process, unlike conventional production methods for carbon tetrachloride, cannot be operated so the perchloroethylene becomes the major product. In many states, perchloroethylene is the only chlorinated solvent permitted in dry cleaning, and the market is likely to be sustained, regardless of any decisions that may be made on aerosol propellants.

There are HCl and phosgene effluents from the chlorolysis process. Neutralization of the effluent streams will produce NaOCl, a compound very toxic to aquatic life.

C. ECONOMIC ANALYSIS

Capital and operating costs for a plant processing 25,000 metric tons/yr of mixed chlorinated hydrocarbon wastes are summarized in Table 2. It was assumed that an average of 3.5 metric tons of CCl_4 would be produced per ton of feed. This is an average of 3.2 tons of CCl_4 per ton of hexachlorobenzene feed, 4.1 per ton of dichloropropane, and 2.4 per ton of hexachlorobutadiene, all typical components of chlorocarbon waste streams.

The capital investment was estimated at about $5.5 million and is based on a figure provided by Hoechst (Ref. 2) of 18 million DM under European conditions for a 50,000 ton/yr commercial plant. Operating costs are calculated as $19,700,000/yr, of which only $890,000/yr represents capital recovery. The cost of chlorine represents 87% of the total annual costs. It is estimated that the process could produce carbon tetrachloride at a cost of 10.2¢/lb, which compares favorably with the current selling price of 19¢/lb.

TABLE 2

ESTIMATED OPERATING COSTS FOR CHLORINOLYSIS

Basis: 25,000 Metric Tons/Yr of Mixed Chlorinated Hydrocarbons
(27,500 Short Tons/Yr) 330 Day/Yr Operation

Estimated Capital Investment – $\$5.5 \times 10^6$

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor	24,000 MH	$12.00/MH	$ 288,000
Maintenance (4% of Inv)			220,000
Chemicals			
Chlorine	137,800 Short Tons	$125.00/ton	17,225,000
Sodium Hydroxide (for scrubber)	800 Short Tons	140.00/ton	112,000
Total Chemicals			$17,337,000
Utilities			
Electricity	11.8×10^6 kWh	$0.02/kWh	236,000
Steam	88×10^6 lb	$\$4.00/10^3$ lb	352,000
Fuel	69.5×10^9 Btu	$\$2.25/10^6$ Btu	157,000
Cooling Water Circulator	2.2×10^9 gal	$\$0.03/10^3$ gal	66,000
Water	109×10^6 gal	$\$0.40/10^3$ gal	44,000
Total Utilities			855,000
TOTAL VARIABLE COSTS			$18,700,000
Fixed Costs			
Taxes and Insurance (2%/yr)			$ 110,000
Capital Recovery (10 Yr – 10%)			890,000
Total Fixed Costs			1,000,000
TOTAL ANNUAL COSTS			$19,700,000
Cost (¢/lb CCl_4 Produced)			10.2
Cost/lb treated waste			$ 0.40

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

The chlorinolysis process seems to provide an efficient, cost-effective means for recovering a salable product from chlorinated hydrocarbon waste streams, assuming that the demand for carbon tetrachloride remains stable.

One factor that might militate against setting up a commercial plant is potential difficulty in securing the waste streams. Just as the average waste recoverer often does not receive all of the waste streams he could effectively process, so the chlorinolysis plant might also experience problems in maintaining adequate sources of supply. The question of legal liability is very important in this connection; there are no clear guidelines as to when a waste generator is no longer responsible for the fate of wastes from his plant. There may also be a problem in obtaining long term commitments for waste feed streams. Changes in chemical processing are not at all uncommon, and usually impact on the wastes available.

It has been suggested that recovery of Cl_2 from the HCl effluent of the chlorinolysis process, and sale of the phosgene, would both improve the economics and the environmental acceptability of the process. Hoechst has a patent for production of Cl_2 from HCl (Ref. 7). The phosgene may not be produced in sufficient quantity to be worth marketing.

If chlorinolysis is a viable process for CCl_4 production, it can be expected to be developed by the commercial sector. Clarification of some of the legal and institutional problems surrounding waste aquisition could stimulate development.

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B. PEOPLE AND/OR ORGANIZATIONS KNOWLEDGEABLE IN THIS FIELD

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DIALYSIS

Prepared by

James D. Birkett

I. CONCLUSIONS AND RECOMMENDATIONS

Dialysis permits certain low-molecular weight or ionic solutes to be "washed" from aqueous streams, using a semi-permeable membrane to maintain separation of the feed and wash streams. The process is slow, capital intensive, and practical only for concentrated feed streams. Both resultant output streams are more dilute than the feed and thus remain as disposal problems, but perhaps aggravated by their increased volume. The only exception would be if reuse is possible.

There is little likelihood of startling technical advances in dialysis so the impact from dialysis on waste treatment may be expected to remain minimal. We recommend that this process not receive attention for industrial waste treatment for the next five years.

II. PROCESS DESCRIPTION

A. BACKGROUND AND UNDERLYING PRINCIPLES

Dialysis is one of several membrane separation procedures, which consist in essence of a barrier which will preferentially pass certain components of a fluid mixture or solution, and a driving force to cause such transfer to take place. Table 1 lists the processes, and the function of the membrane and the type of driving force in each. Dialysis uses a semipermeable membrane capable of passing small solute molecules (such as salts and small organic species) while retaining colloids and solutes of higher molecular weight. The driving force for this transfer is the concentration gradient — the difference in chemical activity of the constituents on either side of the membrane. The transfer through the membrane is by diffusion, that is, the progress of individual molecules, rather than by the hydrodynamic flow that would occur through a porous medium.

TABLE 1

MEMBRANE SEPARATION PROCESSES AND PRINCIPAL DRIVING FORCES

Process	Function of Membrane	Principal Driving Force
Reverse osmosis	Selective transport of water	Pressure
Ultrafiltration	Discriminates on the basis of molecular size, shape, and flexibility	Pressure
Electrodialysis	Selective ion transport	Electrical potential gradient
Dialysis	Selective solute transport	Concentration
Gel permeation chromatography	Retard high molecular weight solute penetration	Concentration
Liquid permeation	Selective transport of liquids	Concentration

Dialysis was first investigated over one hundred years ago as a means of separating colloidal materials from species in true solution. For many years, membranes of animal gut materials were employed, replaced eventually by parchment paper, then rubber nitrocellulose. Today, membranes are of regenerated cellulose (cellophane), and synthetic resin such as polyvinyl chloride. These new materials improve transfer rates and also permit the use of dialysis in more concentrated acid or base media. It has been discovered that interaction of the solvent with the membrane to cause swelling will greatly increase the mobility of solute molecules within the membrane and thus improve transfer rates. This characteristic is particularly exploited in the use of cellulosic membranes in dialysis of caustic solutions, which cause a high degree of membrane swelling.

B. OPERATING CHARACTERISTICS

Requirements for a membrane are good transfer rates, suitable mechanical strength and durability, and resistance to chemical degradation, and low cost. Thermal stability may also be desired, since transport rates for solutes follow the general formula $W = Ae^{-E^*/RT}$ for temperature dependence of diffusion processes and thus there are advantages to carrying out dialysis at somewhat elevated temperatures if possible. The dialysis membranes in most extensive use today are those based upon cellulosic or vinyl materials in either tubular, flat sheet, or recently hollow fiber form.

Although dialysis will occur under "static" conditions, concentration gradients develop on either side of the membrane, and this retards the transfer. To prevent this, it is common practice to provide stirring or high flow rates at the membrane surfaces which minimize stagnant film thickness. Commercial dialysis usually involves the flow of the solute-containing stream across one face of the membrane and the flow of the second higher volume wash stream on the other side (see Figure 1).

Because concentration gradient is the sole driving force, dialysis is generally suited only to concentrated streams (5-20%) in which large concentration gradients may be achieved. Also, the concentration of solute at the feed stream outlet (known as the dialysate) is greater than that of the exiting wash stream (known as the diffusate), except unde. exceptional circumstances.

A water-permeable membrane may experience significant water transfer from the wash stream to the waste stream (an osmotic effect); this tends to diminish the effective concentration gradient. This transfer may be minimized by proper choices of membrane and, when necessary, adding "acceptable" solutes to the wash stream in order to reduce the chemical activity of the water.

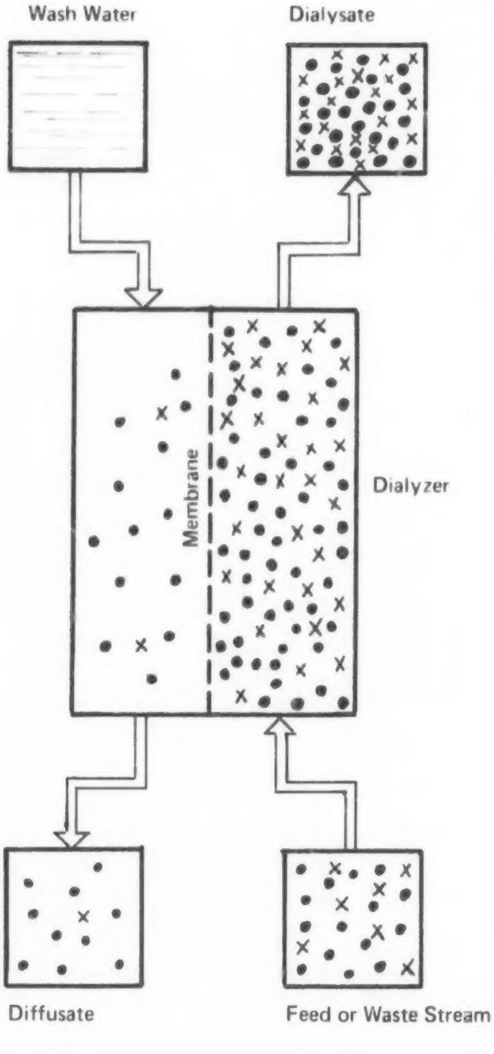

FIGURE 1 SCHEMATIC DIAGRAM OF DIALYSIS

III. APPLICATIONS TO DATE

A. CURRENT PRINCIPAL APPLICATIONS

The best known application of dialysis is hemodialysis, the cleansing of the blood of people suffering from chronic kidney failure. Presently some 20,000 people in the United States undergo a four- to six-hour dialysis three times a week to clear excess salts, urea, and other small molecule wastes from their blood. The membranes used are a special cellophane or regenerated cellulose in film or hollow fiber form and the wash solution is a specially prepared, purified, and sterilized salt solution.

Dialysis has been used extensively since the 1920's in the rayon industry for the separation of caustic soda from hemicellulose waste. Up to 0.85 pounds of caustic are used in the production of a single pound of rayon, and thus there is a large incentive for its recovery. The high concentration (17-18%) of caustic in the feed makes it especially suitable for dialysis of the caustic into the wash stream, while the high molecular weight of the hemicellulose waste restricts its transfer to negligible amounts. The exiting wash stream typically contains highly pure caustic at 8-10%, representing up to 90% recovery. The caustic may be concentrated and recycled; the waste hemicellulose stream must be disposed of.

Dialysis has been used in the electrolytic copper refining industry as a means of separating soluble impurities, such as nickel sulfate, from the spent acid electrolyte after the copper has been removed. A typical spent liquor feed solution may contain 25-30% free acid and 4-10% nickel sulfate. Dialysis through an appropriate membrane into a water stream may permit the recovery of about half of the free acid in a diffusate containing 7-15% acid but only 0.1-0.8% nickel sulfate. This is achieved at transfer rates for the acid as high as 0.4 pounds/hr/ft^2 membrane.

Dialysis has also been used on a smaller scale in pharmaceutical and biochemical laboratories for both special production and purification and for research where it is necessary to separate salts from proteins and other bio-colloids.

Commercial dialysis equipment is presently available from Asaki, Amicon, Brosites, Dow, Graver, and Kooji. Hemodialysis equipment is manufactured by Cordis-Dow, Travenol, Extra-Corporeal, Gambro-Lundia, and other suppliers.

B. POTENTIAL APPLICATIONS TO WASTE TREATMENT

The potential applicability of dialysis to hazardous wastes is limited to liquids containing high concentrations of low-molecular weight dissolved species. (In theory, it could be useful in nonaqueous systems, assuming a compatible membrane material, but this does not seem to have been investigated.) Caustics and the mineral acids dialyze readily, although oxidizing materials, such as nitric or chromic acid, or spent etchants, may cause severe membrane degradation unless they are properly chosen. Because of their small size, one would expect cyanides to permeate the membrane fairly well. Particulate matter which could plug the flow system or cause membrane erosion should be removed by a pretreatment, as should any constituents which might tend to form sludges or films on the membrane surfaces.

We have not been able to identify any actual applications of dialysis to hazardous waste disposal problems, other than those industrial applications mentioned above which promote some recycling of potential wastes. Wherever membrane filtration is employed, users choose reverse osmosis, ultrafiltration, electrodialysis, or some other similar process.

The disadvantages of dialysis are its low rate, its unsuitability to dilute feed solutions (less than 0.1%), and the fact that both output streams are more dilute than the feed, and thus the material to be disposed of would require additional concentration.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements for dialysis are minimal; since the transfer is driven by the chemical concentration gradient, the only energy input is for low-pressure pumping of the feed solution through the device.

B. ENVIRONMENTAL IMPACTS

There is no air pollution from dialysis; however there are two diluted streams which must be reused or further treated prior to disposal.

C. ECONOMIC ANALYSIS

Dialysis is generally capital intensive, involves only modest labor (principally maintenance), and uses very little energy.

Capital costs are based on the amount of waste to be removed, rather than upon waste stream throughput, and thus cost can vary greatly from installation to installation. As an indication of capital costs, let us consider a solute having a dialysis transfer coefficient of two pounds per hour/square foot/gram per cubic centimeter (concentration), a value comparable to that of a mineral acid in a vinyl membrane. If the effective concentration gradient in the system is designed to be 0.1 g/cc (i.e., 20% vs 10%) the transfer rate will be 0.2 pound per hour per square foot. Thus if the model calls for the salvaging of 1000 pounds of solute per day, 210 ft^2 of membrane will be required. Such a commercial dialyzer would cost (assuming $15 per square foot for a unit using "conventional" membrane materials) about $3000, independent of any necessary pretreatment of the feed. However, half of the solute would not be reclaimed, would be further diluted and thus still present some disposal problems.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

As dialysis is a mature technology, no "breakthroughs" are expected. Although under certain conditions dialysis may be tied to a reuse or concentration process, these applications are rare. By itself, dialysis is not a likely candidate for hazardous waste treatment, and we recommend that it not be given further analysis in the evaluation of treatment methods. It should be assigned to Category I.

There is little likelihood that this process will be useful for industrial waste treatment in the next 5-10 years.

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DISSOLUTION

Prepared by

James R. Valentine

I. CONCLUSIONS AND RECOMMENDATIONS

Dissolution is a preliminary or first treatment step that can be used to remove either major or minor constituents from solids. The major output from the process is a liquid stream containing the hazardous components that must be subjected to further processing for recovery or destruction. The process is applicable to any solids or mixture of solids that can be wetted by the suitable liquid.

We recommend that emphasis be placed on more complete characterization of solids to aid in the specification and testing of possible dissolution processes for these solids. Furthermore, in view of the sensitivity to chemical costs, efforts should be made to utilize lower quality or waste reagents wherever possible.

II. PROCESS DESCRIPTION

A. BACKGROUND

Dissolution reactions are used in nearly all areas of chemical processing. In general, these reactions are carried out to accomplish one (or both) of two goals — namely, to remove one or more components from a solid mixture, or to cause a solid to transfer into a liquid phase in order to effect a chemical reaction that would be difficult or impossible to carry out in the solid phase.

Dissolution reactions have been employed purposefully in hydrometallurgy, an area related to hazardous waste treatment, since the 1800's, and in the synthetic chemicals industry since its inception.

There are many areas in waste treatment where dissolution may be employed to advantage, and most of these involve wastes that are primarily inorganic in nature. Accordingly, this report is focused principally on the utilization of dissolution for the treatment of inorganic materials, with some reference to the potential for use with organics.

B. UNDERLYING PRINCIPLES

Dissolution may be defined as the complete or partial transfer of one or more components from a solid phase into a liquid phase in contact with the solid. The liquid phase may consist of an active consumable reagent in a carrier solvent or a simple solvent alone. The carrier solvent used most frequently in dissolution of inorganic species is water because it aids in holding the dissolved species in solution (i.e., it "solvates" the dissolved species), and is by far the most common and inexpensive solvent.

The dissolution reaction involves some degree of chemical transformation (solvation, ionization, oxidation) of the species being dissolved. The driving force for the reaction is the formation of a more stable solvated species or the transformation (more or less non-reversible), of one of the species by a reagent. An example of the former is the selective dissolution of water-soluble ("leachable") salts from an otherwise water-insoluble solid, while an example of the latter is the dissolution of a water-insoluble metal carbonate salt in an acid, brought about with the formation and evolution (loss) of carbon dioxide from the solution.

The only limits to the performance of dissolution are the necessity for providing a sufficient amount of reagent to react (stoichiometry requirement) and providing sufficient solvent so that the solubility limit for the dissolved species being formed is not exceeded.

C. OPERATING CHARACTERISTICS

1. Acceptable Feed Streams

Dissolution involves transfer of one or more components of a solid phase into a liquid phase, and, in theory the process can be applied to any solid containing a species of interest capable of being dissolved.

Forms of solids that are acceptable include:

a. Dry solids, such as:
  - metallic wastes (metal machining waste)
  - dry powders (flue dust, flyash)
  - ashes (incinerator, coal combustion)

b. Slurries, such as:
  - scrubber slurries
  - metal machining slurries (electrochemical machining, for example)
  - sludges (hydroxide and liming sludges from metal finishing processes, frequently having solids contents in the 1 to 10% range)

c. Organics, such as:
  - Metallized and metal-containing polymer wastes

The range of acceptable concentrations includes:

a. Solids where the major components are to be dissolved, principally for recovery of those components;

b. Solids where only minor components are to be removed for eventual destruction, stabilization or possible recovery.

There are no upper or lower limits to the concentration or amounts of substances that can be removed by dissolution provided that sufficient reagent is added to satisfy the stoichiometry requirements, and that sufficient solvent is added to maintain the concentration of the dissolved species below the solubility limit.

Since the solids must be capable of being wetted by the solvent, excessive oil and grease and other hydrophobic substances must be removed either prior to dissolution processing in water or aqueous solvents or by addition of suitable detergents to the dissolution solvent.

2. Process Operation

In the dissolution process the solids are contacted with the reagent in a mixer for a length of time determined by the kinetics of the particular reaction taking place, following which the slurry is separated. Heat may be applied to speed up the process and to provide increased solubility.

Terminology common to the metallurgical industry is useful for differentiating the various phases, since in that industry, as in virtually any waste treatment process, only a part of the solids are being dissolved. The dissolution reaction is frequently referred to as "leaching" or "lixiviation," and the solvent is the "leach liquor" or "lixiviant." The solids are termed the "pulp" and the unwanted portion of the solids, which remains behind after leaching, is the "gangue."

There are various modes of operation, or methods of contacting the solids. A brief description of these is given below.

- **Batch Leaching**

  This process involves loading the mixer with appropriate amounts of solids and lixiviant, mixing until leaching is complete, and then separating the phases. Next to percolation, this is the simplest mode of leaching, and is used in waste processing.

- **Co-current Continuous Leaching**

  This process involves the continuous addition of both solids and lixiviant (in the proper proportion) to a stirred mixer, and discharge of the same proportions. These units run at a steady-state point where the composition of the discharge corresponds to some percentage of the total leaching possible (i.e., the final composition of the batch leach). By cascading two or more co-current leaches, and varying the residence times in each if necessary, it is possible to achieve a continuous discharge from the final mixer that is equivalent to a batch leach. In addition to providing a continuous output, this mode of operation is generally more efficient in reagent consumption than batch operation, and as a consequence yields a leach liquor that is freer from undesired species. This mode is widely used in large scale hydrometallurgical leaching.

- **Countercurrent Continuous Leaching**

  This process involves counter flow of both liquid and solids. This system affords the maximum efficiency of lixiviant usage. Because of the necessity to separate the phases after each stage countercurrent continuous leaching is practiced infrequently, and generally only when the pulp contains a high proportion of leachable species.

- **Percolation Leaching**

  This is a process in which the leach liquor passes down through a column or pile of the solid, and is collected at the bottom. This process resembles a countercurrent batch process. Since it frequently requires little labor and equipment, the process is widely used for leaching very low grade ores.

The solids can be treated with two or more lixiviants sequentially, for selective removal of different species. This can be particularly useful where removal of a valuable component will result in simultaneous leaching of undesirable materials. For example, a solid composed of the mixed hydroxides of nickel, copper and chromium (III) can be leached initially with ammonium carbonate to remove nickel and copper, and then the chromium can be removed with a sulfuric acid leach (Refs. 4,5).

Separation of liquors and solids is generally accomplished using thickeners and filters. The modes of operation are more fully explained in many texts available on hydrometallurgy practice (Refs. 1 and 3, for example).

As noted previously, this report is concerned principally with dissolution of inorganic materials in aqueous lixiviants. Dissolution of organic materials in organic solvents would be carried out in a similar mode, the major difference being the possible need for control of vapor emissions.

Another type of dissolution process involves the use of fused salts as solvents. Such materials have been used as chemical reaction media, and have some useful solvent and electrochemical properties. However, the energy cost and large amounts of salts required make their use in waste processing highly unlikely at this point.

3. Output Streams

Dissolution differs markedly from most other waste treatment processes in that the major intended product is an aqueous stream that will always require further treatment for separation, recovery, stabilization or destruction of the species leached from the solids.

After being washed to remove entrained leach liquor, the residual solids (gangue) may be suitable for disposal, re-use or for further waste treatment processing.

D. EQUIPMENT AND MATERIALS

1. Equipment

Dissolution operations make use of common mixing and separating equipment such as is in use in the hydrometallurgical area (Refs. 1, 3, 6).

- Mixers include both impeller driven and air-lift (pachuca) types.
- Separating equipment includes thickeners and various filters. The reports on separation equipment in this study will give more information on that category of equipment.

Materials of construction should be appropriate for the solvent being used. Extremely corrosion resistant materials (titanium for example) may be required for processes designed to recover corrosion resistant alloys from machining wastes (Ref. 7).

2. Reagents

A wide variety of reagents can be used. However, economics dictate that only a very few will have much utility in waste processing. The major categories of reagents are as follows. Obviously, if reagent materials of acceptable quality can be had as wastes, then the potential cost savings could outweigh a somewhat poorer performance than would be expected from pure solvents.

- Acids – Sulfuric, hydrochloric, nitric, phosphoric, and carbon dioxide are all useful to one degree or another in the dissolution of basic salts (hydroxides, oxides, carbonates) of metals. Sulfuric is by far the most widely used; hydrochloric where complexing is needed; carbon dioxide is used with ammonia in leaching copper and nickel.
- Bases – Sodium hydroxide is the principal base; however, lime and sodium sulfate can also be used to yield dilute solutions [$Ca(OH)_2 + Na_2SO_4 \rightarrow 2NaOH + CaSO_4$]. Sodium hydroxide is used to dissolve metallic aluminum.
- Complexants – Ammonia, ammonium salts, and sodium cyanide are used commercially as leaching agents for copper and nickel from ores.
- Oxidants – Air (O_2), chlorine; air has been used frequently as an oxidant in leaching of copper ores; chlorine finds use with hydrochloric acid in dissolving corrosion resistant metals such as cobalt/nickel alloys.

III. APPLICATIONS TO DATE

A. HISTORICAL APPLICATIONS

As mentioned previously, dissolution in its most general sense has been practiced purposefully since the inception of the chemical industry. Applications in hydrometallurgy, which in many respects resemble waste treatment, came into practice in the late 1800's.

B. PRINCIPAL CURRENT APPLICATIONS

1. Hydrometallurgy

Dissolution is practiced widely in the hydrometallurgical recovery of many different metals from ores, ranging from base metals such as copper to exotic materials such as uranium.

There is a large body of information on such applications and it would be inappropriate to attempt to summarize such results in this report except where a point pertinent to waste processing may be made.

The leaching reagents and conditions employed depend to a great extent on the nature and chemical composition of the ore being treated. For example, copper oxides and carbonates can be leached with acids or ammonia (as the carbonate or sulfate salts), while copper sulfides require an oxidant (such as oxygen) in order to destroy the sulfide in addition to a complexing agent such as ammonia. Copper metal ("native" copper) requires an oxidant (such as air) and a complexant (such as ammonia) in order to oxidize the element to the copper (II) oxidation state (Refs. 1-3).

Likewise, certain uranium ores are acid-leachable while others can be leached with sodium carbonate (Ref. 3). Pretreatment of ores, ranging from grinding to roasting under oxidizing or reducing conditions, to convert the metals to more accessible forms is widely practiced in processing of various metals.

Without going into further detail it is obvious from the efforts expended in the hydrometallurgical processing of many ores that each ore is different and may require quite different treatment conditions.

2. Waste Treatment

In contrast to the widespread usage of dissolution processes in the chemical process industries, and in hydrometallurgy, there appear to be relatively few instances of commercial practice in waste treatment. However, there is an understandable reluctance on the part of some waste processors to disclose any information relating to such a potentially competitive area. Nearly all reported commercial operations involve dissolution of bulk materials for recovery rather than selective stripping of minor constituents.

One application (at Western Processing Co.) involves the production of various zinc and iron chemicals for agricultural and other uses by dissolving skimmings from galvanizing operations and flue dusts containing zinc and iron in waste acids (Refs. 8,9). Commercially valuable products realized from the processes include zinc sulfate, zinc ammonium sulfate, ferrous ammonium sulfate, and ferric sulfate. The reactions are carried out in batch operations.

A commercial operation (at Capital Wire and Cable Co.) for the recovery of metallic copper scrap involves dissolution of the material in ammonia/ammonium carbonate solution with air oxidation (Refs. 11,12).

A semi-commercial scale plant was reportedly being considered in Sweden for recovery of copper, nickel, and zinc from plating slimes. (Ref. 13). The solids, which are reported to be a mixture consisting almost entirely of hydroxides of copper, nickel, zinc, iron and chromium, are dissolved in sulfuric acid.

C. PILOT AND LABORATORY SCALE INVESTIGATIONS IN WASTE PROCESSING

There are a variety of pilot and laboratory studies of waste processing operations which utilize dissolution as a preliminary step. As in the commercial applications, nearly all the processes involve recovery of major constituents. A few processes representative of the dissolution techniques used are listed below.

1. Zinc, copper, nickel and chromium can be recovered from slags and ashes by leaching with a mixture of sulfuric and nitric acids, the latter being necessary to promote oxidation (Ref. 13). Unused nitric acid in the leach liquor is recovered for reuse by a solvent extraction step.

2. An extensive, continuing study of the recovery of copper, nickel and chromium from electroplating waste sludges is being carried out at Battelle Columbus Laboratories (Refs. 4,5). These sludges, most of which result from the liming of wastewater, contain low percentages of these metals and are highly variable even within a given sludge. Some recent results for leaching of a typical sludge with various reagents are summarized below to illustrate the variability in composition and in leaching behavior.

Nominal range of metal content of sludge (dry basis):

Copper: 5-9%
Nickel: 0.9-1.0%
Chromium: 13-17%

Leaching Reagent	Materials Leached Out
50% H_2SO_4	Virtually all Cu, Ni and Cr removed, plus 40-60% of solids
20% H_2SO_4	Virtually all Cu, Ni and Cr removed, plus 30-60% of solids
very strong $(NH_4)_2CO_3$	Appr. 60% Cu, 90^+% Ni and Appr. 5% Cr
dilute $(NH_4)_2CO_3$	∿ 35% Cu, ∿ 50% Na and ∿ 4% Cr
conc. NH_4OH	∿ 30% Cu, 5% Ni and 2% Cr
H_2O	10% of solids (Ca and Na salts)

The Battelle study has shown that some selectivity in leaching can be had by utilizing reagents which have been used for recovery of copper and nickel from ores. However, the results for the ammonium salt leaches indicate that extraction of copper and nickel from these sludges is not nearly as effective as with previously studied copper and nickel ores (Ref. 5).

3. Cobalt and nickel can be leached by sulfuric acid (Ref. 7) from wastes such as spent catalysts and sludges.

4. Metallic wastes of nickel and cobalt alloys can be dissolved in hydrochloric acid using chlorine as the oxidant (Refs. 7,14).

In nearly all cases where relatively expensive reagents such as hydrochloric acid, nitric acid or ammonia are used, the processes are designed to recover and recycle as much of the reagent as possible.

Prior leaching of the waste with water has been shown to be beneficial for some wastes in order to minimize the amount of unwanted salt removed during the active leaching. For example, in the Battelle work (see above) one sludge contained at least 10 percent water extractable solids (Ref. 5), while leaching of spray-dried sludges from electrochemical machining removed a large amount of sodium chloride and nitrate (for recovery) and yielded a dry solid containing 50 percent recoverable metals as opposed to 10% in the unleached material (Ref. 7).

D. DISSOLUTION PROBLEMS PECULIAR TO WASTE PROCESSING

As mentioned previously, development of dissolution and leaching processes for treatment of ores has been predicated in general upon a reasonably constant composition of the feed solids and, obviously, large volume operations. While some general technology for selective leaching may be transferrable between solids of similar composition further testing and refinement is generally necessary in order to optimize recovery (i.e., removal) and economics. The problem of transferring dissolution methodology from material to material is compounded in waste processing, because in general very little is known about the composition and contents of the waste. This problem is illustrated very well by the work at Battelle on metal sludge leaching cited above. Sludges that were somewhat similar in composition behaved rather differently during leaching (Ref. 4), and even sludges from the same source varied markedly in metal content and in leaching properties (Ref. 5). As pointed out previously, techniques used for ores of supposedly similar composition did not work as well as expected with sludges.

In order to cope with these problems, it may be necessary to employ more energetic general leaching operation (strong acids, strong oxidants) than desirable. Even so, having more information on the solids composition would enable a more knowledgeable selection of possible reagents and conditions before starting tests. These composition data must include all major substances, as well as the components to be dissolved, and should include chemical identity of the latter where possible.

Some thought must also be given to treatment prior to dissolution. While grinding and milling may be too expensive for waste treatment, a simple mixing may improve homogeneity of the material, thereby ensuring that leaching conditions established on one portion will be applicable to all others.

E. POTENTIAL APPLICATIONS IN WASTE TREATMENT

As pointed out above, dissolution is applicable to a wide variety of waste forms and qualities. Present commercial and laboratory applications have centered around those wastes that have sufficient metal value for economic recovery. The area of selective leaching for removal of small amounts of hazardous substances has had little work to date and should be looked at more closely.

Selective leaching with even moderately expensive reagents may prove useful for the removal of trace impurities on solids as for example in the removal of trace hazardous metals and metalloids (lead, cadmium, arsenic, selenium) from flyashes and flue dusts.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

The energy requirements for dissolution are relatively minor, principally electricity for mixing and pumping, and possibly steam or other source of heat if required to aid the dissolution process. The driving force for the reaction is principally chemical.

B. ENVIRONMENTAL IMPACTS

The dissolution process involves both solids and liquids, and may also involve gases under certain circumstances.

- Emissions to water will not be significant provided that the liquors used and produced are properly conveyed to the next processing step with no inadvertent losses.
- No land disposal problems are anticipated provided that any leached solids which have been made suitable for landfill disposal are adequately washed to remove leach liquor prior to such disposal.
- Emissions to air will be significant only when there is gas evolution occurring during dissolution. Such gas evolution may be the result of the intended dissolution reaction such as release of carbon dioxide during dissolution of carbonates in acid, or of an unintended reaction such as reaction of traces of sulfides in the water to give hydrogen sulfide.

There are no special land use factors associated with the usual modes of dissolution, although percolation leaching through heaps or piles of material may require some extra space.

The only safety problems that might arise involve handling the loaded leach liquor and reagents.

C. ECONOMIC ANALYSIS

Because of the diversity of materials which may be subjected to dissolution, and the range of reagents and conditions that might be required to handle any particular material, an approximate economic analysis was made for a hypothetical waste in order to demonstrate the sensitivity of the process to chemicals, labor and capital costs.

- Feed Stream – dry, mixed metal liming sludge solids from metal finishing, 10,000 lb/day, containing:

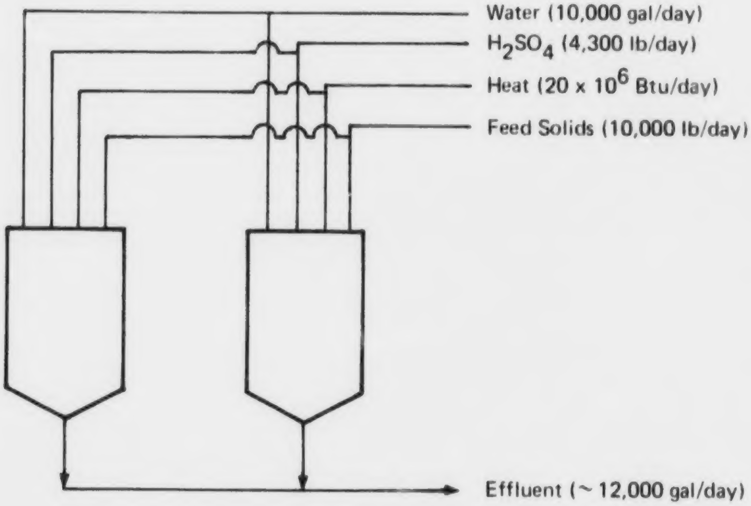
  copper – 3.2%
  nickel – 3.6%
  chromium – 7.3%
  zinc – 5.6%
  cadmium – 0.4%

  chemical form of metals and remainder of solids are unspecified

- Treatment Objective – to dissolve all of the metals listed above.

- Design Basis – dissolution in aqueous sulfuric acid, 10% solids, 93°C; batch operation – 24 hours/day – 350 days/year; 2 reactors @ 1100 gal each (stainless steel); 4 hour mix time, 5 batches/day

  Note: process includes dissolution only, *not* separation


Water (10,000 gal/day)
H_2SO_4 (4,300 lb/day)
Heat (20 x 10^6 Btu/day)
Feed Solids (10,000 lb/day)
Effluent (~ 12,000 gal/day)

Costs are detailed in Table 1.

The estimates are very approximate but are sufficient to confirm a point that is well established in hydrometallurgy practice, namely that such processes are extremely chemical intensive.

The cost for clean sulfuric acid is $24/ton of solids processed, or approximately 40% of the processing costs. If there are any extraneous acid-consuming substances present such as excess lime or sodium carbonate, then obviously the acid consumption will be increased in proportion to the content of those substances.

Use of clean acid reagents other than sulfuric will result in even higher reagent costs, and may also require special corrosion resistant equipment. A comparison of prices of various clean reagents on the basis of cost per mole of active species is given in Table 2. The use of air for oxidation is also obviously to be preferred to even the least expensive oxidant.

TABLE 1

COST ESTIMATES FOR DISSOLUTION TREATMENT SYSTEM

Variable Costs	Annual Quantity	Unit Quantity	Annual Cost
Operating Labor	2200 Mh	$ 12.00/hour	$ 26,400
Electricity	300,000 kWh	0.02/kWh	6,000
Heat	7 x 10^9 Btu	$2/$10^6$ Btu	14,300
Chemicals			
H_2SO_4	750 tons	53.25/ton	42,750
H_2O	3.5 x 10^6 gal	0.20/100 gal	700
Maintenance (3%)			2,400
Total Variable Costs			$ 92,550
Fixed Costs			
Taxes and Insurance* (2%)			$ 1,600
Capital Recovery* (10%-10 years)			13,200
Total Fixed Costs			$ 14,800
Total Operating Costs			$107,000

*Estimated Capital Investment – $80,000

Unit Cost	($/ton of input solids)	$ 61
	($/ton of desired metal removed)	$300

Source: Arthur D. Little, Inc., estimates.

TABLE 2

REAGENT PRICE COMPARISON

Reagent	$/T for New Reagents (May 1976)	$/kg Mole of Active Species
H_2SO_4 (100%)	53.25	2.86
HCl (32%)	33	4.14
HNO_3 (100%)	125	8.65
NaOH	180	7.92
$Ca(OH)_2$	34.50	1.41
NH_3	180	3.37
Cl_2	150	11.70

Waste processing offers ample opportunity to utilize waste reagents that frequently are available at substantially lower cost. In general, the cost of such reagents is related to the nature and amount of impurities present including dilution with water and other solvents. In some cases, the producers of such wastes will pay to have them removed. Examples of waste reagents are waste acids (sulfuric or hydrofluoric) from petrochemical alkylation processes and waste hydrochloric acid from chlorination processes.

Such waste reagents can be utilized in many treatment processes where the impurities contained in the reagents will not interfere with subsequent processing steps, or result in the necessity for additional processing steps. For example, dilute sulfuric acid contaminated with heavy metals probably could be used for leaching of metal-containing sludges without problem. However, sulfuric acid containing much organic matter, as is often found in spent alkylation acid, might well introduce sufficient organics into the process stream to upset subsequent separation steps such as precipitation or ion exchange. In addition, the organics thus added might necessitate an additional treatment step in order to render the aqueous stream suitable for discharge or reuse.

Judicious choice of waste reagents could lower treatment costs significantly. In the ADL economic example, use of "free" sulfuric acid would lower the treatment cost to $37/ton of input solids.

A smaller batching operation should not be much more costly to operate.

The reagent costs represent the minimum possible costs even for leaching in a heap in a lined hole in the ground such as is employed in recovering copper from very low grade ore. Heap leaching is unlikely to be acceptable for waste treatment, however.

No other cost estimates for waste processing have been found to date, generally because dissolution is used only as a first step in a series of processing operations.

V. OUTLOOK FOR DISSOLUTION IN INDUSTRIAL WASTE TREATMENT

A. BENEFITS AND LIMITATIONS

Pollution Potential	Little likelihood of water pollution if operations properly performed no land pollution if undissolved solids are washed some air pollution potential from gases evolved during leaching.
Classes of Waste	Will handle any solid that can be wetted and dissolved most suitable for inorganics
Breadth of Applicability	Preliminary treatment only, hazardous materials transferred into solution.
Operational Feasibility	Already demonstrated on metallic and metal salt wastes.
Economics	Probably a minimum of $300/ton of metal value removed, very sensitive to excessive reagent requirements.
Energy	Only minor amounts of mixing, and some heating if required.
Time Requirements for Development	Already in use.

B. MODIFICATIONS OR IMPROVEMENTS THAT WOULD BE BENEFICIAL

Process equipment and operations are already in a high state of development. More work needs to be done on understanding the composition of various sludges and mixed metal compounds in relation to leaching behavior.

C. RECOMMENDATIONS

Emphasis should be placed on more complete characterization of solids to aid in the specification and testing of dissolution processes that might be employed on these solids.

In view of the sensitivity to reagent costs, efforts should be made to utilize lower quality or waste reagents where possible.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

1. Waste Treatment Users

Western Processing Co., Kent (Seattle), Washington, Mr. Garmt J. Nieuwenhuis
Capitol Wire and Cable Co., Casa Grande, Arizona

2. Waste Treatment Research and Development Studies

Battelle Columbus Laboratories, Columbus, Ohio, Dr. Robert H. Cherry, Jr.
U.S. Bureau of Mines, Metallurgy Research Center, Salt Lake City, Utah.
MX Processer AB, Molndal, Sweden, Dr. Hans Reinhardt.
Warren Spring Laboratory, Stevenage, England, Dr. Douglas S. Flett, Dr. D. Pearson

3. Hydrometallurgy Experience

There are many companies that are actively engaged in hydrometallurgy practice and research such as:

Kennecott Copper Corp. (process laboratories in Salt Lake City, Utah).
AMAX, Inc. (laboratories in Salt Lake City, Utah).

DISTILLATION

Prepared by

Lawrence R. Woodland

I. CONCLUSIONS AND RECOMMENDATIONS

Distillation is a unit operational process which is most often employed in industry to segregate, separate, or purify liquid organic product streams, some of which contain aqueous fractions. Sometimes the operation is used to recover one product; sometimes it is used to produce many desirable fractions from a process stream. Distillation is usually non-destructive and can produce products of any desired composition. Practical limitations are primarily economic ones, i.e., both operational and equipment costs.

Until now, organic solvent recovery has been justified only when the economics warranted it. However, with the recent enforcement of stringent air pollution regulations, most organic solvents are prohibited from entering the atmosphere. This is being accomplished in a number of ways, such as direct condensation, demisting, absorption, etc. Often, regeneration of absorption media produces aqueous and/or organic streams. Distillation is often employed to recover the organics.

In the recovery of other waste solvents such as painting or plating wastes or plastic coating wastes, distillation cannot directly compete with other recovery or with disposal processes. However, this can be offset when favorable byproduct credits exist. With more and more stringent regulations on air, liquid effluents, and land site disposal, the rising cost of organic chemicals (i.e., increased byproduct credit), and the newer concept of waste management (resource recovery), distillation should become more competitive with other methods for liquid organic recovery or disposal.

II. PROCESS DESCRIPTION

A. BACKGROUND

The basic principle of distillation is as simple as it is old: when a liquid solution is boiled, the vapor usually differs in composition from the liquid that remains. Man has long made use of this knowledge to concentrate solutions by boiling them and condensing the vapors that are driven off. The distillation of what are essentially binary (two-component) mixtures of ethanol and water has been practiced by brewers and distillers for centuries. It has only been since the 19th Century, however, that distillation has been developed on a large-scale basis as a steady-state operation. The major contributions in this field have come from engineers in the petroleum industry, where large numbers of multistage distillation towers operate on a continuous basis.

B. UNDERLYING PRINCIPLES

Distillation is the boiling of a liquid solution and condensation of the vapor for the purpose of separating the components.

In the distillation process there are two phases, the liquid phase and the vapor phase. The components which are to be separated by distillation are present in both phases but in different concentrations. If there are only two components in the liquid, one concentrates in the condensed vapor (condensate) and the other in the residual liquid. If there are more than two components, the less volatile components concentrate in the residual liquid and the more volatile in the vapor or vapor condensate.

The ease with which a component is vaporized is called its volatility, and the relative volatilities (ratio of equilibrium ratios) of the components determine their vapor-liquid equilibrium relationships. (See Figure 1 for a typical vapor equilibrium curve.)

Equilibrium Ratio – An equilibrium ratio expresses a relationship between a vapor and a boiling liquid in physical equilibrium with one another. For each component, $y = K_x$, in which "y" is the mole fraction* of a particular component in the vapor state, "x" is the mole fraction of that component in the liquid state, while "K" is termed the equilibrium ratio. For any system, there are as many such relationships as there are components.

Relative Volatilities – Because distillation separates by virtue of inequalities in volatilities, equilibrium ratios are less important than are their relationships to each other. These secondary relationships are termed "relative volatility." The relative volatility (α_{AB}) of component A to component B is defined by $\alpha_{AB} = K_A/K_B$.

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*Mole fraction is the ratio of the number of molecules of a particular component to the total number of molecules of all the components in a phase.

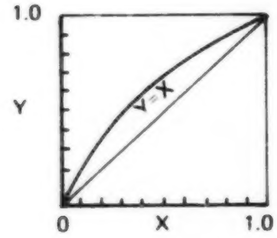


FIGURE 1 TYPICAL EQUILIBRIUM CURVE WHERE X IS THE MOLE FRACTION OF THE COMPONENT IN THE LIQUID STATE AND Y IS THE MOLE FRACTION IN THE VAPOR STATE."K" CAN BE DETERMINED AT ANY POINT BY CALCULATING $\frac{Y}{X}$

The numerical value of the relative volatility (α_{AB}) is significant to the direction and to the degree in which the separation of the components will take place. If $\tilde{\alpha}_{AB}$ is equal to (numerical) one, this means that the mixture is azeotropic (see Figure 2), (i.e., there will be no difference in the composition between the liquid and the vapor at equilibrium) and it cannot be separated by ordinary distillation methods. (Azeotropic distillation will be discussed in Section II-C.) If α_{AB} is less than one, then component B is the more volatile of the two components and will be more concentrated in the vapor phase and leaner in the liquid phase. If α_{AB} is more than one, then the reverse will be true. The degree to which the separation will take place under a given set of equilibrium conditions depends on how far the relative volatility deviates from (numerical) one.

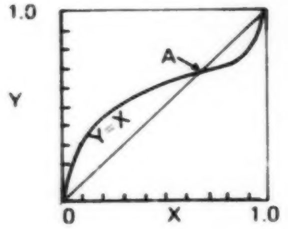


FIGURE 2 TYPICAL EQUILIBRIUM CURVE FOR AN AZEOTROPIC SYSTEM WHERE X IS THE MOLE FRACTION IN THE LIQUID STATE AND Y IS THE MOLE FRACTION IN THE VAPOR STATE."A" DENOTES THE AZEOTROPIC POINT$\left(K = \frac{Y}{X} = 1\right)$

C. TYPES OF DISTILLATION PROCESSES

1. Batch Distillation

The simplest form of distillation is a single equilibrium stage operation and is carried out in a "still" in which the reboiler equivalent consists of a steam jacket or a heating coil. The liquid is "boiled"; the vapor is driven off, condensed, and collected in an accumulator (a condensed vapor collector) until the desired concentration of the "product" has been reached. As the remaining liquid becomes leaner in the volatile component and richer in the less volatile component, its volume diminishes. If the residual liquid is the product, then "bottoms" concentration will be the controlling parameter.

The batch still, as previously described, consists of a vessel which provides one equilibrium stage. By adding a condenser and recycling some of the condensed vapor, a second vapor/liquid equilibrium stage is added and the separation is improved (Figure 3).

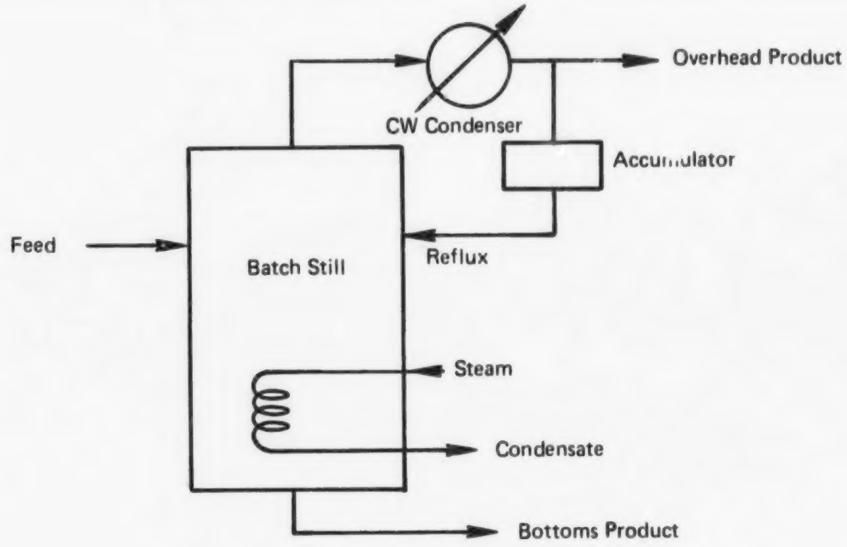


FIGURE 3 BATCH FRACTIONATION WITH REFLUX AND INTERNAL HEATING COIL

2. Continuous Fractional Distillation (Figure 4)

A steady stream feed enters the column. The column contains plates or packing (packing is normally used only in small-scale equipment) which provide additional vapor/liquid contact (equilibrium) stages. Overhead vapors and bottoms are continuously withdrawn. Vapor from the top plate is condensed and collected in a vessel known as an accumulator. Some of the liquid in the accumulator is continuously returned to the top plate of the column as reflux while the remainder of the liquid is continuously withdrawn as the overhead product stream.

At the bottom of the column the liquid collects in the reboiler, where it is heated by steam coils or a steam jacket. The function of the reboiler is to receive the liquid overflow from the lowest plate and return a portion of this as a vapor stream, while the remainder is withdrawn continuously as a liquid bottom product.

3. Azeotropic Distillation (Figure 5)

An azeotrope is a liquid mixture that maintains a constant boiling point and produces a vapor of the same composition of the mixture when boiled. Boiling point diagrams of azeotropes are illustrated in Figures 6 and 7. The first figure applies to a mixture of chloroform and acetone, a maximum-boiling-point azeotrope; the second to mixtures of benzene and ethanol, a minimum-boiling-point azeotrope. In either curve, the upper line is called the dew point, i.e., the point at which the vapor begins to condense, and the bottom line the bubble or boiling point, i.e., the point at which the component begins to vaporize. In Figure 7, the boiling point t_b corresponds to concentration x_a, the lowest boiling temperature reached by any mixture (minimum-boiling-point azeotropes), and is lower than that of either pure component. The reverse is true for a maximum-boiling-point azeotrope. Of the two types, minimum-boiling-point azeotropes are more common.

Because the composition of the vapor produced from an azeotrope is the same as that of the liquid, an azeotrope may be boiled away at a constant pressure, without change in concentration in either liquid or vapor. Since the temperature cannot vary under these conditions, azeotropes are also called constant boiling mixtures.

An azeotrope cannot be separated by constant pressure distillation into its components. Furthermore, a mixture on one side of the azeotrope composition cannot be transformed by distillation to a mixture on the other side of the azeotrope. If the total pressure is changed, the azeotropic composition is usually shifted. Sometimes this principle can be applied to obtain separations under pressure or vacuum that cannot be obtained under atmospheric pressure conditions. Most often, however, a third component – an additive, sometimes called an entrainer – is added to the binary (2-component) mixture to form a new boiling-point azeotrope with one of the original constituents. And the volatility of the new azeotrope is such that it may be easily separated from the other original constituents.

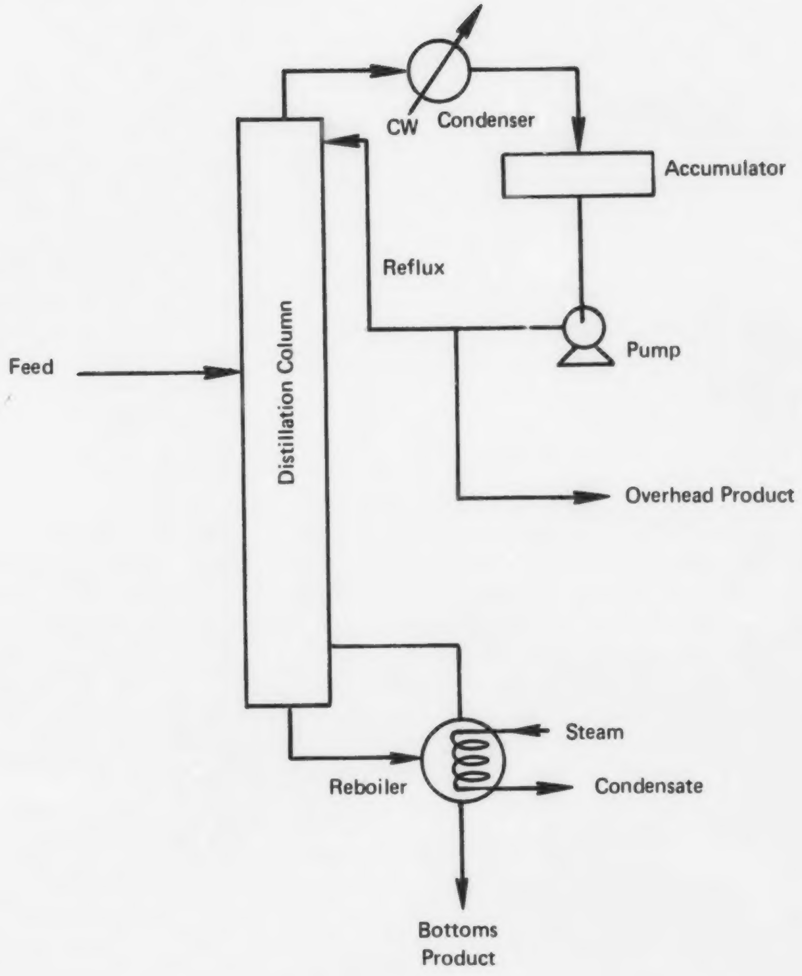


FIGURE 4 CONTINUOUS FRACTIONAL DISTILLATION COLUMN

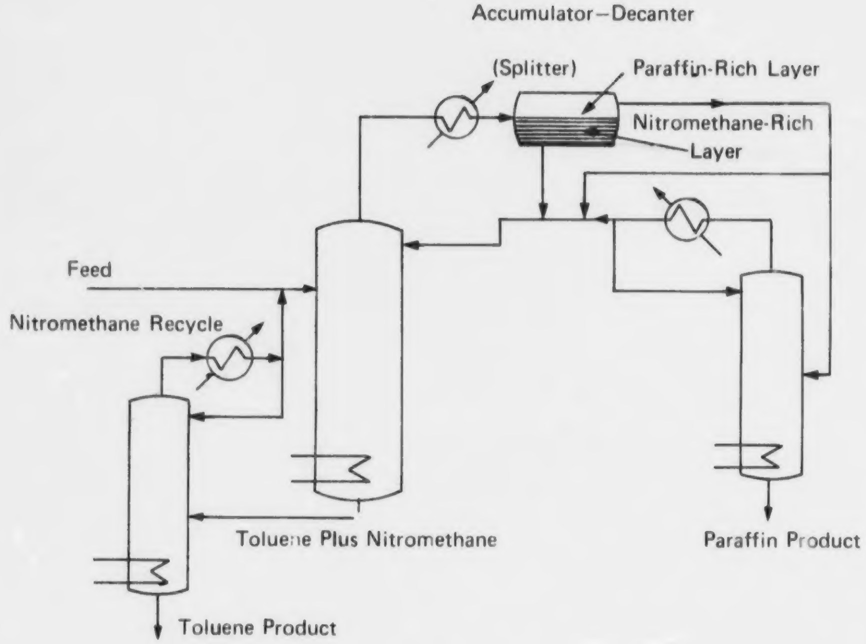


FIGURE 5 FLOW SHEET FOR AZEOTROPIC DISTILLATION OF A PARAFFIN-TOLUENE MIXTURE WITH NITROMETHANE AS AN ADDED AGENT

4. Extractive Distillation (Figure 8)

This is a multi-component rectification method of distillation. A solvent is added to a binary mixture which is difficult or impossible to separate by ordinary means. This solvent alters the relative volatility of the original constituents, thus permitting separation. The added solvent is of low volatility and is not appreciably vaporized in the fractionator.

5. Molecular Distillation

Molecular distillation is a form of a very low pressure distillation conducted at absolute pressures of the order of 0.003 mm of mercury suitable for heat-sensitive substances. Ordinarily, the net rate of evaporation is very low, at a safe temperature, owing to the fact that evaporated molecules are reflected back to the liquid after collisions occurring in the vapor. By reducing the absolute pressure to values used in the molecular distillation, the mean free path of the molecules becomes very large (in the order of 1 cm). If the condensing surface is then placed at a distance not exceeding a few centimeters from the vaporing liquid surface, very few molecules will return to the liquid and the net rate of evaporation is substantially improved.

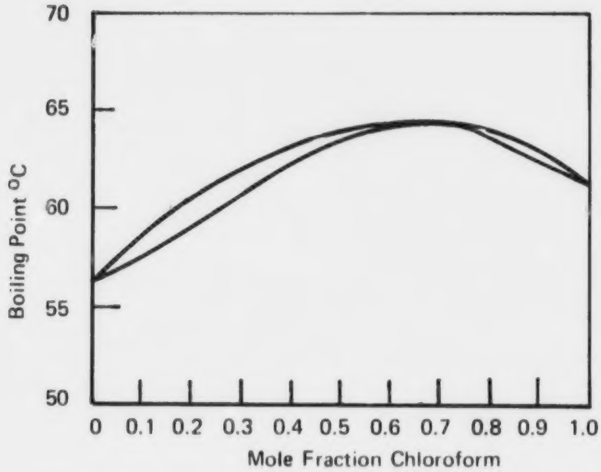


FIGURE 6 BOILING-POINT DIAGRAM SHOWING MAXIMUM-BOILING AZEOTROPE (SYSTEM CHLOROFORM-ACETONE)

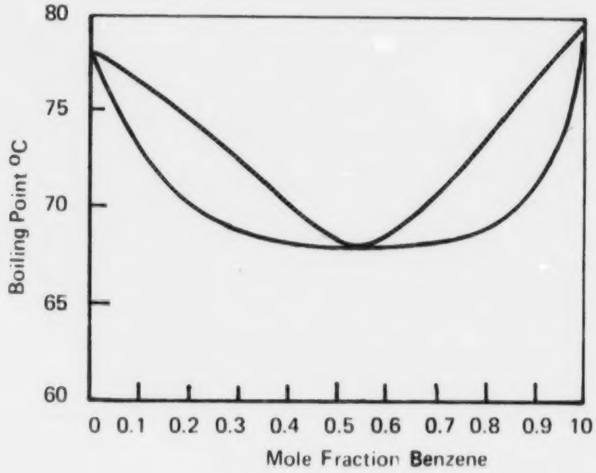


FIGURE 7 BOILING-POINT DIAGRAM SHOWING MINIMUM-BOILING AZEOTROPE (SYSTEM BENZENE-ETHANOL)

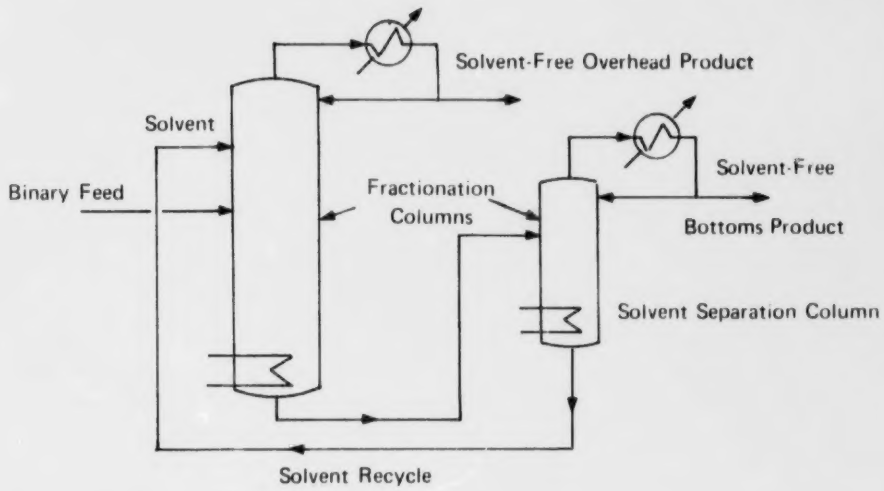

Solvent-Free Overhead Product
Solvent
Binary Feed
Fractionation Columns
Solvent-Free Bottoms Product
Solvent Separation Column
Solvent Recycle

FIGURE 8 TYPICAL FLOW SHEET FOR AN EXTRACTIVE DISTILLATION PROCESS

D. OPERATING CHARACTERISTICS

Although the term distillation is sometimes employed for those processes in which a single constituent is vaporized from a solution, e.g., in "distilling" water, this term is properly applied only to those operations in which vaporization of a liquid mixture yields a vapor phase containing more than one component, and it is desired to (1) recover one or more of the components in a nearly pure state or (2) obtain a mixture different from that of the original mixture. Thus, the separation of a mixture of alcohol and water into its constituents is accomplished by distillation, whereas the separation of brine into salt and water is evaporation, even in those cases where the salt is not desired and the condensed water is the valuable product.

1. Feed Streams

It is preferred that the materials being distilled do not contain appreciable quantities of solids or non-volatile materials. It is also best to avoid feeds that tend to polymerize.

The presence or formation of these contaminants in the feed can cause considerable operating difficulties. Operation of a conventional distillation system on a feed which is "dirty" could cause plugging of equipment or costly maintenance problems. This could precipitate in inefficient separation of feed components or produce excessive "flooding" conditions. This is a situation in which the vapor rate is reduced nearly to zero because of increased pressure drop in the vapor caused by having to travel through deep layers of liquid. Another effect might be long downtime periods required for equipment cleaning.

If it is known in advance that feeds of this nature must be handled, steps can be taken to design equipment which would minimize the associated problems (e.g., sieve-type trays might best be able to handle liquids which contain tars). Sometimes, steps can be taken to avoid the problem completely – such as pretreatment by filtration, for removal of suspended solids or the use of a thin film evaporator to separate the volatile (liquid) fraction from the solid or non-volatile component(s). When the problems associated with "dirty" feed cannot be easily handled or are unavoidable, duplicate equipment may be the only answer. This measure prevents disruption in production. When one set of equipment is down for cleaning or maintenance, the other system can take over operation.

In terms of physical separation of liquid components, there are no limitations in feed composition or in reaching the desired composition in any of the product streams. Theoretically, distillation can generate products of 100% absolute purity. There are, however, some physical parameter restrictions, such as entrainment effects, which limit the degree of attainable purity to the (10^{-9} to 10^{-14}) range of impurities. The attainment of these limits of purity is usually not necessary, nor are the limits normally attempted, because of requirements of highly specialized equipment, extreme equipment size, excessive capital investment, or energy considerations.

2. How Distillation Operates

a. Fractionation

The term "fractionation" (see Figure 9) means separation of a material into its component parts where more than one part is a desired product, while the term "distill" is sometimes used, in the colloquial sense, to mean the driving off of a volatile component and the collection of the condensed volatile liquid as the one product (e.g., the distilling of alcohol from a water-alcohol mixture). In distillation, the term "fractionate" means to separate a liquid feed into a series of fractions containing different ratios of the components present in the original feed.

b. Feed

The liquid (or vapor) being introduced into the distillation column is called "feed." The section of the column above the feed location is called the enriching or rectifying section. In this section, the more volatile component is concentrated. The portion of the column below the feed location is the stripping section. Here the liquid becomes richer in the less volatile component as the more volatile component is removed (stripped).

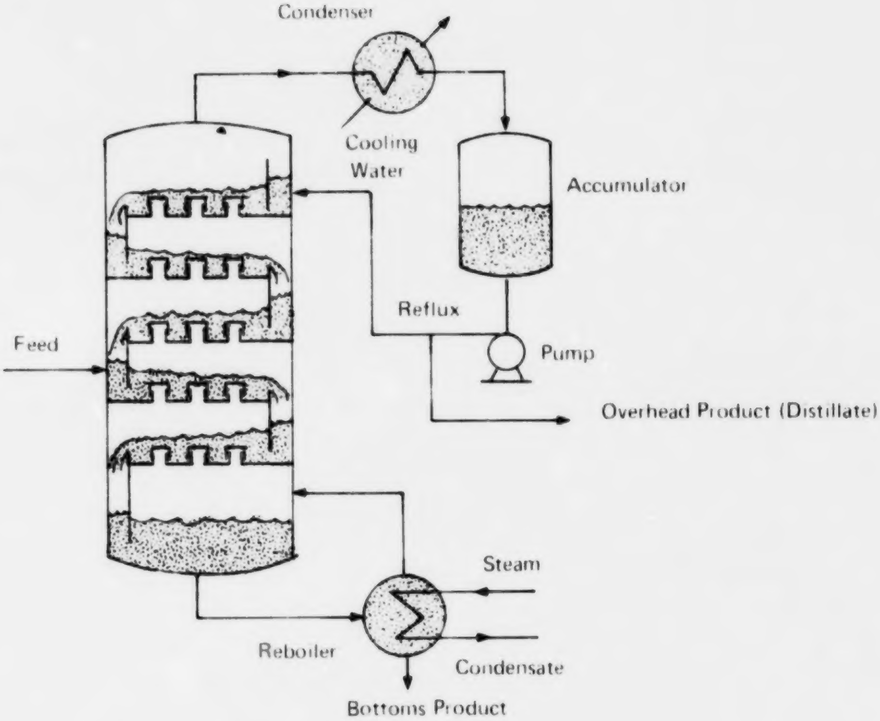


FIGURE 9 SCHEMATIC DIAGRAM OF OPERATION OF A FRACTIONATING COLUMN CONTAINING BUBBLE-CAP PLATES

(1) Binary Liquid Feed — In the case of distillation, a binary system consists of two liquid components in solution with one another.

(2) Multi-component Liquid Feed — In multi-component distillation, the liquid being processed is composed of more than two components.

c. Equilibrium Stage

An "equilibrium stage" occurs when the liquid and the vapor phases are in equilibrium with one another. This equilibrium may occur on a single tray or plate (or within a given height of packing in a packed column) where the rising vapor and falling liquid (condensed vapors) contact each other.

d. Non-ideal Stages

In an ideal, or equilibrium stage the phases are mixed long enough so that the streams leaving the stage are in equilibrium, and the individual phases are homogeneous (i.e., there are no concentration gradients). By contrast, in a real stage there may not be sufficient contact between the phases to bring the streams into equilibrium. Such a stage accomplishes less interphase transfer than an ideal stage; it is less efficient than an ideal stage. The degree to which a stage approaches ideality is termed "stage efficiency."

3. Output Streams

a. Bottoms Product

The liquid recovered from the bottom of the column is called "bottoms." It is generally richer in the less volatile components. The term "still bottoms" refers to the undesirable non-volatile residue materials, such as tars and sludges, which are periodically removed from the reboiler or from the bottoms product tank. These materials, which usually enter with the feed or are sometimes formed to a slight degree by polymerization reactions, must generally be disposed of.

b. Overhead and Overhead Product

The vapor which is evolved at the top of the column is called the "overhead." All or part of the overhead may be withdrawn as product. This is called "overhead product." The overhead product may be withdrawn as a vapor or condensed and collected as a liquid.

c. Reflux

When all or part of the overhead is recycled back to the column (usually to the top stage or plate), that recycled portion is termed "reflux."

d. Reflux Ratio

This term can either refer to the ratio of the reflux to feed, or to the overhead product. In compliance with the more general usage, this text will refer to the latter.

E. EQUIPMENT AND MATERIALS

1. Distillation and Fractionation Columns

The types of distillation columns are so varied they defy concise description. The distillation process could be carried out in wide cylindrical columns up to 40 feet or more in diameter, or in tall columns 200 feet high (or more) in the air, or even in small laboratory equipment.

a. Rectifying Columns (See Figure 10)

These are fractionating columns in which the feed enters the bottom of the column as a vapor. An overhead product is produced which is usually quite rich in the more volatile component while the bottoms product contains a high proportion of the less volatile component.

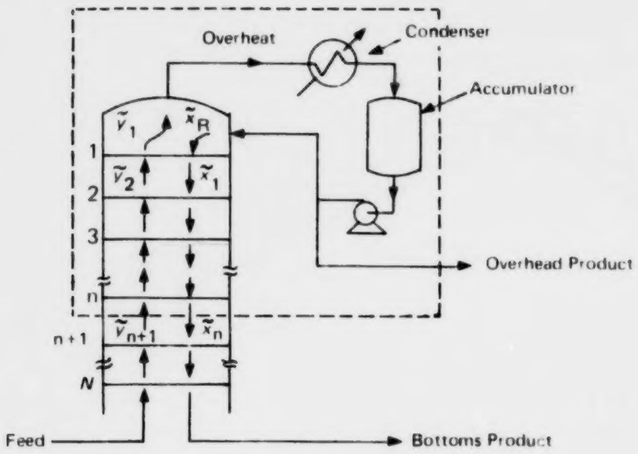


FIGURE 10 OPERATION OF A RECTIFYING COLUMN WITH CONSTANT OVERFLOW WHERE N = NO. OF STAGES

b. Stripping Columns (See Figure 11)

These are fractionating columns in which the liquid feed is supplied to the top of the column. The feed is usually a saturated liquid, and the overhead product is the vapor rising from the top plate. This vapor is somewhat richer in terms of the more volatile component than is the feed. However, it is usually not a stream of very great purity. The only stream leaving the stripping column that has a very high concentration of a component (the less-volatile) is the saturated-liquid bottoms product.

c. Complete Fractionating Columns (See Figure 12)

When a column has a section both above and below the feed injection point, a possibility exists of producing both rich overhead and bottom products. Thus, the complete fractionating column combines the properties of both enriching and stripping columns. The complete column has both a reflux condenser and a reboiler.

(1) Column Internals

To facilitate mass transfer, commercial columns always contain internals that provide for increased vapor to liquid interfacial area. The designs of these internals are many and varied. By convention, the various internals are grouped into two broad classifications: trays and packings.

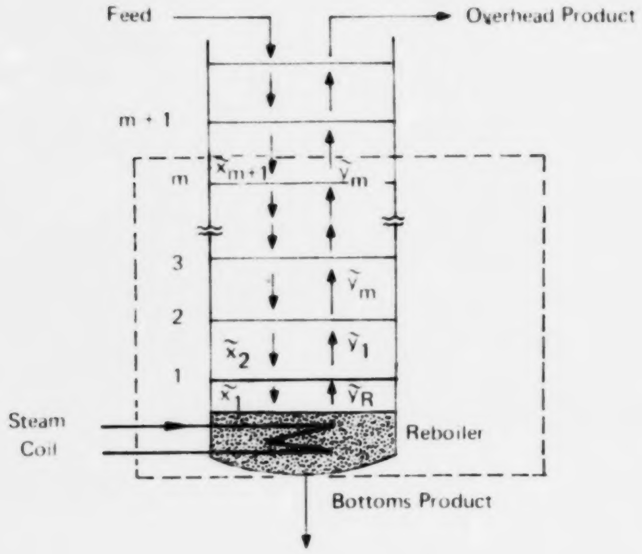


FIGURE 11 OPERATION STRIPPING COLUMN WITH CONSTANT OVERFLOW WHERE M = NO. OF STAGES

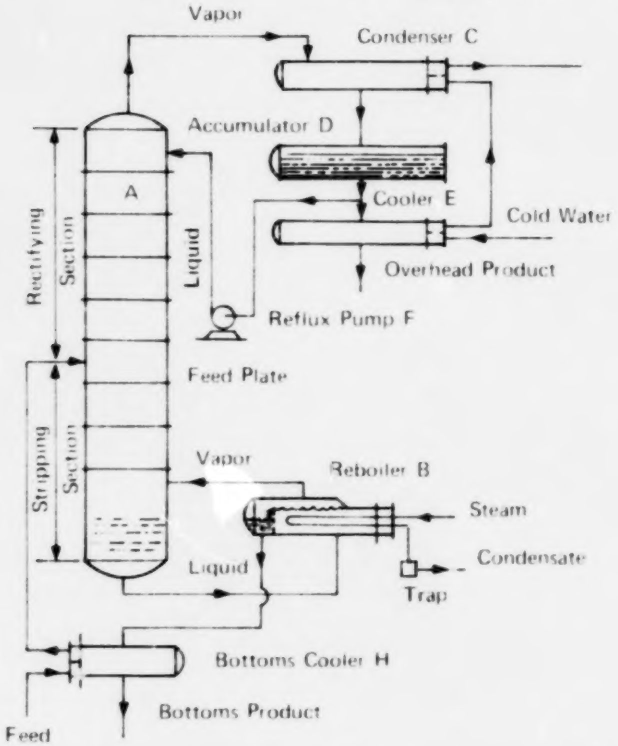


FIGURE 12 A TYPICAL CONTINUOUS FRACTIONATING COLUMN EQUIPPED WITH THE NECESSARY AUXILIARIES AND CONTAINING RECTIFYING AND STRIPPING SECTIONS

(a) Distillation Trays (See Figures 13-15) A distillation tray is a horizontal plate that holds a pool of the downflowing liquid through which the upflowing vapor passes. To permit passage of the vapor, the plate must have openings of some kind. Depending on the design, liquid may flow down through the same openings that the vapor is flowing up through, or it may flow across the plate to a vertical "downcomer" (a channel or pathway that directs the liquid to the next lower tray).

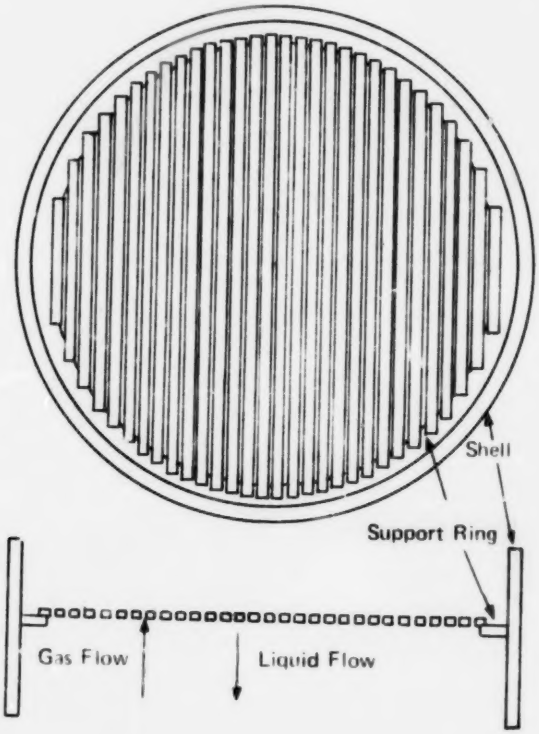


FIGURE 13 AN EXAMPLE OF A SIMPLE TYPE OF TRAY-TYPE CONTACTING DEVICE

(b) Packing (See Figures 16-18) Like trays, packings are installed in distillation columns to improve the contacting of the downflowing liquid with upflowing vapors. Originally, "packing" meant small, irregular solids that, when installed in a random fashion, left irregular passages for countercurrent travel of vapor and liquid. Currently, packings are so diverse that the only inclusive definition is: vapor-liquid contacting devices not classified as trays.

All packings function by providing surface area over which the downflowing liquid distributes itself, thus increasing the area of the liquid-vapor interface. Some packings function as do trays in that they promote the formation of pools of liquid through which the vapor bubbles.

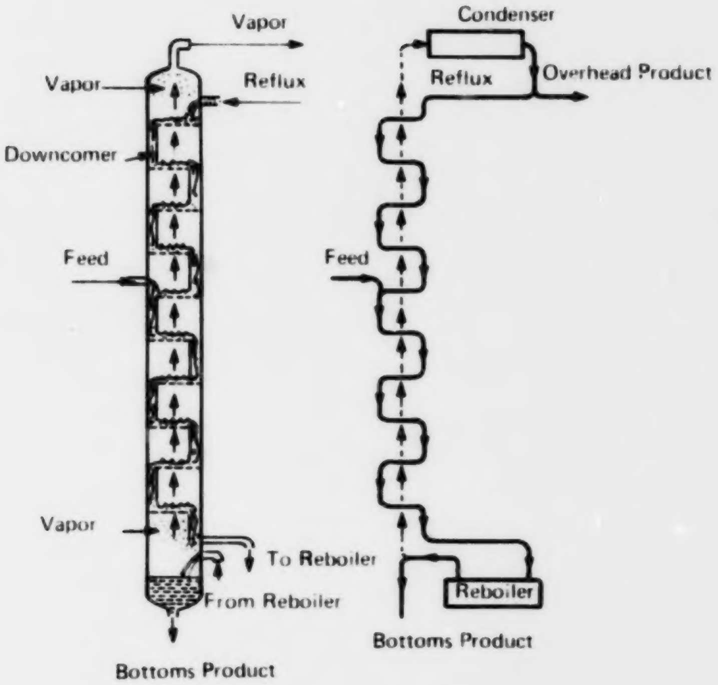


FIGURE 14 OPERATION OF A TRAY COLUMN

In most packed distillation columns there are liquid redistribution plates to counteract liquid channeling. They are normally located at intervals equivalent to three to five column diameters.

(2) Column Construction

(a) Integral Shell An integral-shell column is one in which the shell is one continuous piece, with trays or packing supports which are welded to the shell. This type is used in high pressure applications where thick-walled columns are required. This kind of shell type is used in almost all petroleum refining operations and in many others where mild steel or other ferrous alloys are satisfactory materials of construction.

(b) Flanged Shell Flanged shell columns are composed of flanged cylindrical sections, each containing five or six trays. The trays are usually single sheets of metal turned up at the edges and slipped into the column. They are not fastened to the shell. Instead, the tray is supported by vertical posts that rest on the next lower tray.

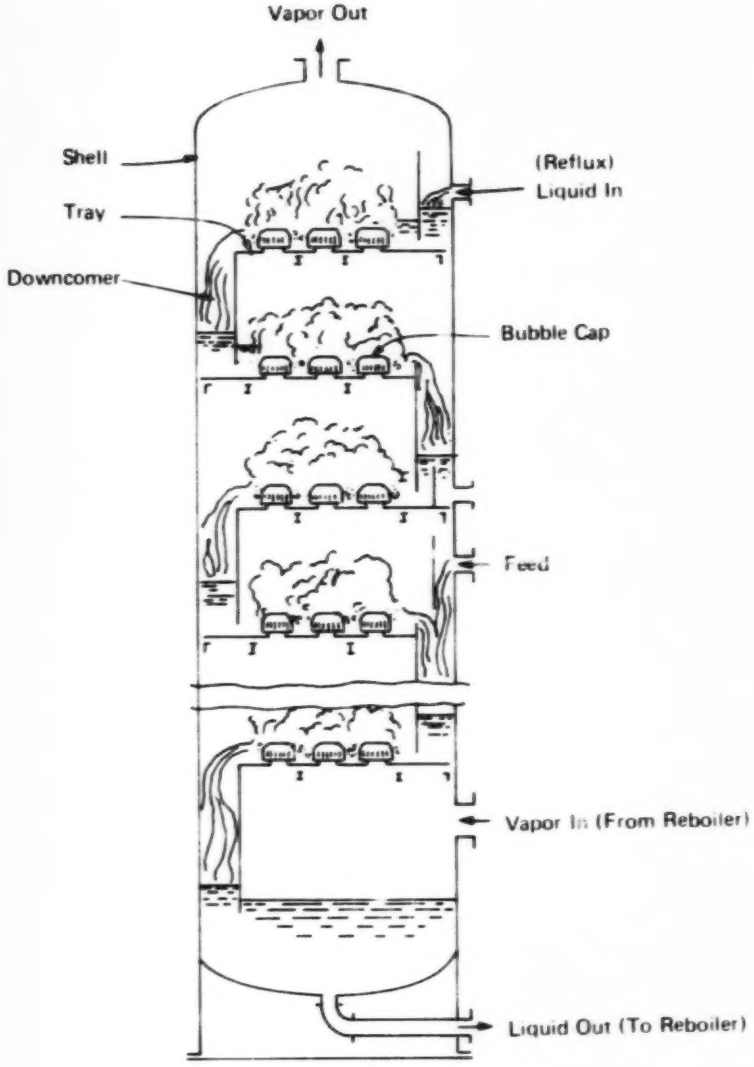
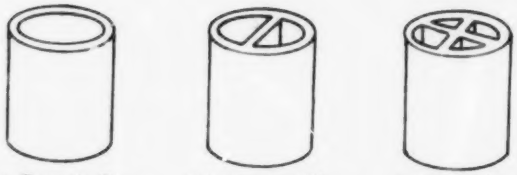
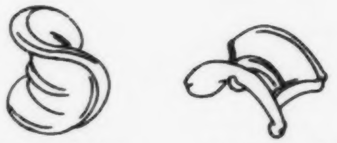


FIGURE 15 SCHEMATIC DIAGRAM OF BUBBLE-CAP TRAY TOWER



(a) Raschig Ring (b) Lessing Ring (c) Partition Ring



(d) Berl Saddle (Courtesy, Maurice A. Knight)

(e) Intalox Saddle (Courtesy, United States Stoneware Co.)

FIGURE 16 RANDOM TOWER PACKINGS

2. Reboilers

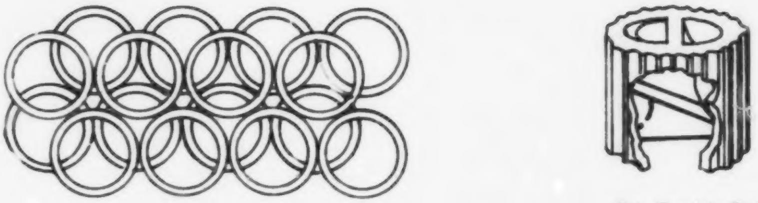
Energy is required to vaporize the liquid phase. Heat is applied to the liquid phase to provide the energy of vaporization. This energy may be applied externally to the column by circulating liquid from the column through a heat exchanger called a reboiler. Sometimes a vapor is employed as the heat exchange medium (as in steam distillation), and sometimes the column is jacketed and the heat transfer medium is circulated in the vessel jacket.

3. Condensers

Energy must be removed to condense the vapor phase. This is usually provided via a heat exchanger (condenser) through which a cooling medium is passed or circulated. Sometimes, part of the energy used to heat up or partially vaporize the liquid phase that is to be distilled is "recovered" from the condensing vapor phase.

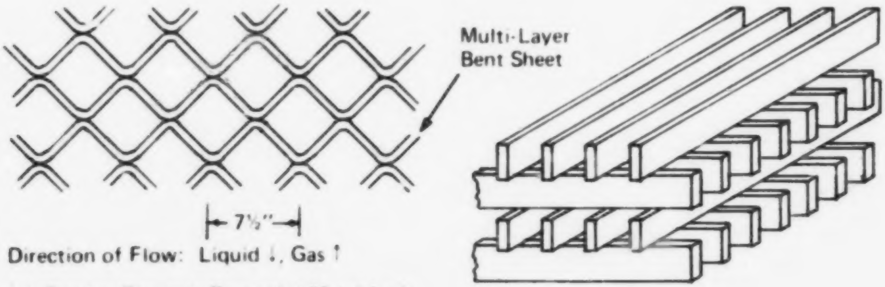
4. Accumulators

The accumulator is a tank located on the downstream side of the overhead vapor condenser. Its purpose is to collect the condensed vapor, as a small intermediate storage vessel. This helps to promote stability of operation.



(a) Raschig Rings, Stacked Staggered (Top View)

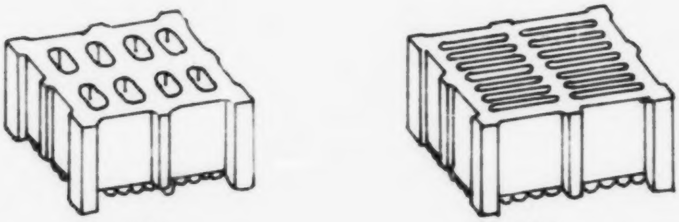
(b) Double Spiral Ring (Courtesy, United States Stoneware Co.)



Direction of Flow: Liquid ↓, Gas ↑

(c) Section Through Expanded Metal Lath Packing[21]

(d) Wood Grids



No. 6146

No. 6295

(e) Drip-Point Grids (Courtesy, General Refractories Co.)

FIGURE 17 REGULAR, OR STACKED, TOWER PACKINGS

5. Pumps

Most of the pumps employed in modern distillation units are either the centrifugal or the rotary type. Rotary pumps are often employed when the liquid contains suspended solids, but special centrifugal pumps have given good service in the pumping of slurries.

6. Vacuum Equipment

Vacuum equipment could be either steam jet eductors or mechanical vacuum pumps. Eductors have high reliability and low capital cost compared to mechanical vacuum pumps; this is offset, however, by relatively low efficiencies and high operating costs.

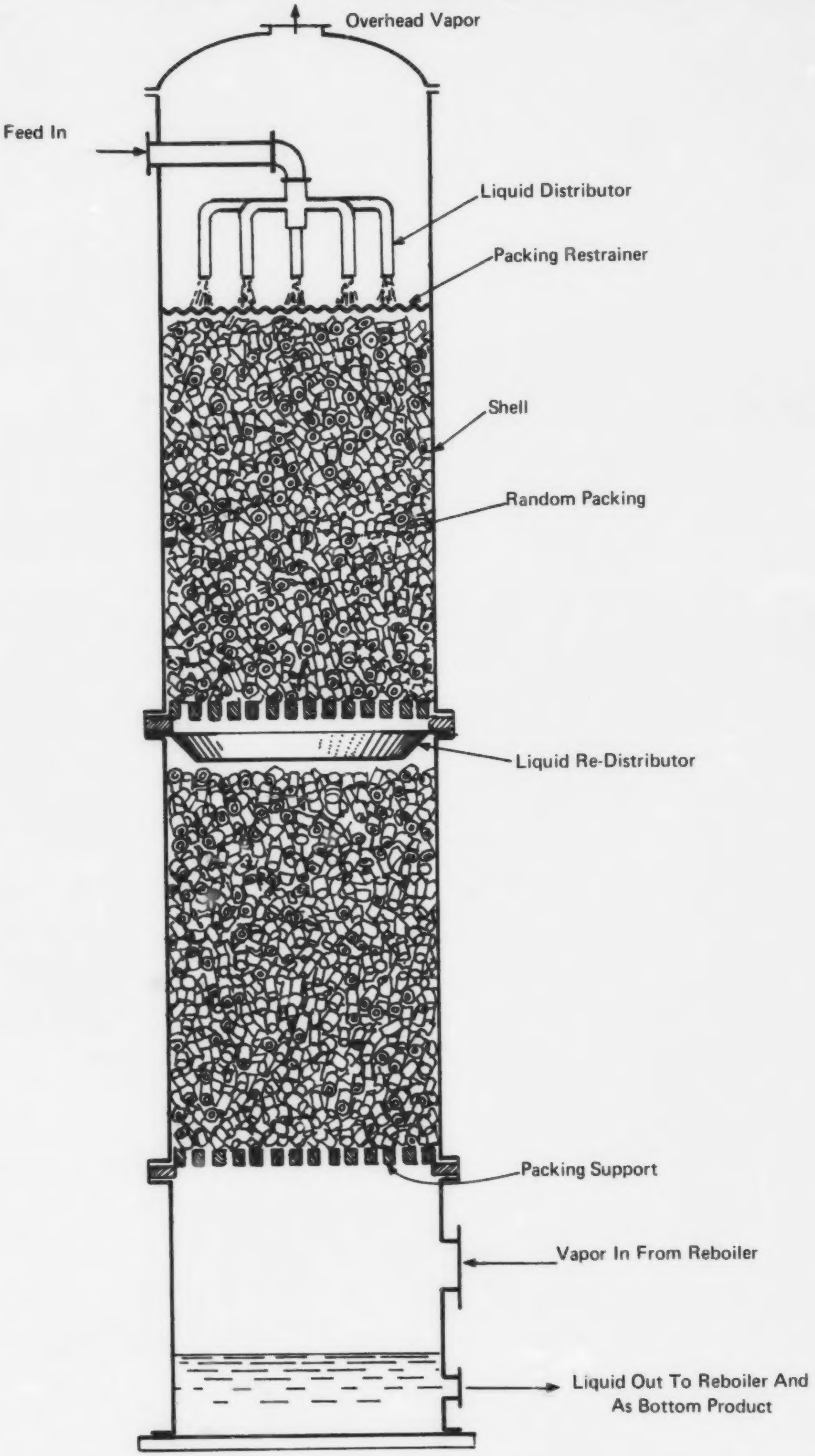


FIGURE 18 A PACKED TOWER WHICH IS USED FOR CONTINUOUS COUNTERCURRENT CONTACT OF LIQUID AND VAPORS HAS BEEN FILLED WITH PACKING OR DEVICES OF LARGE SURFACE CONTACT AREA

7. Maintenance Provision Equipment

Because maintenance can constitute a substantial operating cost, maintenance considerations are important. These include: layout of equipment, design of supporting structures, and provision of auxiliary items such as davits.

III. APPLICATIONS TO DATE

A. GENERAL INDUSTRIAL APPLICATIONS

Distillation has wide industrial application. Very often in the production of organic liquids, the products are not in the pure state. Rather, they are contaminated with undesirable components or combinations of organic chemicals and byproducts. To separate the desirable products, or fractionate the chemical from its secondary byproducts, distillation is employed. This can either be a single operation or part of a treatment sequence.

Some typical industrial applications include:

General	**Specific**
Petroleum fractionation	Petroleum refining of gasoline, fuel oil, etc.
Organic chemical purification	Removal of unreacted cresols in the manufacture of TCP
Organic chemical intermediate manufacture	Chlorobenzene separation
Solvent recovery	Recovery of acetone from an acetone/water waste stream
Cryogenic separation	Air separation plants producing oxygen, nitrogen, and argon

Materials which cannot generally be treated by distillation are organic peroxides or pyrophoric organics and inorganic wastes. If waste streams which contain "gunk" (i.e., viscous, thick, gooey, polymeric materials, tars, etc., and combinations thereof) must be treated by distillation, the streams should receive preliminary treatment, if possible, to remove these materials, as they may tend to severely foul the equipment. If this is not possible, then special equipment may be required.

For example, one waste disposer treats paint solvent wastes by use of a special direct steam-injected reboiler with rotating internal parts. This prevents the "gunk" from solidifying and causing major equipment maintenance problems. His "still" bottoms, however, contain large quantities of organic solvents; this presents a disposal problem. Another waste processor treats the same type of waste with a system having duplicate shell and tube reboilers. When one reboiler is shut down for reaming and cleaning of the tubes, the other reboiler takes over. A third solvent reclaimer, who treats paint solvent wastes, has made no special equipment modifications, but he must shut down his distillation equipment for extended periods while the cleanup procedures take place. Occasionally, his reboiler becomes so fouled-up that all the heating surfaces must be replaced. The latter two processors have a much lower level of contained solvent in their "still" bottoms, but their equipment, operational, and maintenance problems contribute to a considerable portion of reclaiming costs. Treating the solvent waste with a thin-film, scraper blade evaporator prior to the distillation offers another method for removing materials that would interfere with the distillation.

B. INDUSTRIAL WASTE TREATMENT APPLICATIONS

Perhaps because of the cost of the energy requirements, treatment of waste by distillation is not widespread. The only hazardous waste materials which can be feasibly and practicably treated are liquid organics, including organic solvents and halogenated organics, which do not contain appreciable quantities of materials that would cause operational or equipment problems.

There are a number of manufacturers of chemicals and chemical products who have always recovered solvent streams by distillation for internal reuse. There are also a number of independent operators and companies which specialize in solvent or chemical reclamation by distillation. Historically, distillable solvents have been recovered primarily as an economic consideration, but with imposition of more stringent government regulations for the disposal of hazardous wastes and increases in the cost of petrochemicals, byproduct credits will become even more important. Thus, the recovery of organic solvents should become more prevalent. If byproduct credits offset the higher cost of distillation, vs. the cost of other recovery methods, distillation will become a more competitive means of waste solvent recovery.

The solvent reclaiming industry pertains to those private contractors engaged in the reprocessing of organic solvents. In many cases, these operations also include other means of reclamation such as steam-stripping evaporation, filtration, etc. Table 1 contains a partial listing of independent processors and waste solvent distillers.

Typical industrial wastes which can be handled by distillation:

- Plating wastes containing an organic component – usually the solvents are evaporated and the organic vapors distilled.
- Organic effluents from printed circuit boards are adsorbed on activated carbon. Regeneration of the activated carbon gives a liquid which is distillable for recovery of the organic component.
- Phenol recovery from aqueous solutions is a major waste treatment problem. The recovery process uses a polymeric adsorber. The adsorber is regenerated using a vaporized organic solvent. A complex distillation system is used to recover both the regeneration solvent and the phenol. See Figure 19.
- Methylene chloride which contains contaminants is a disposal problem, but it can be salvaged for industrial application by distilling.
- Methylene chloride can be recovered from polyurethane waste.
- The separation of ethylbenzene from styrene and recovery of both.
- Waste solvents for reuse in cleaning industrial equipment. Usually a mixture of acetone (ketones) (alcohols) and some aromatics.

TABLE 1

EXAMPLES OF INDEPENDENT PROCESSORS AND WASTE TREATMENT DISTILLERS

Chemical Exchange Company
Houston, TX

CPS Chemical Company
Old Bridge, NJ

Chemical Processors, Inc.
Seattle, WA

Conservation Chemical Company
Kansas City, MO

Waste Research and Reclamation Company, Inc.
Eau Claire, WI

Rodgers Laboratories, Inc.
Milwaukee, WI

Chemical Waste Disposal Corporation
Astoria, NY

Chem-Trol Pollution Service Inc.
Subsidiary of SCA Services Inc.
Model City, N.Y.

National Convertors, Inc.
Union, NJ

Marisol, Inc.
Middlesex, NJ

Silresim Chemical Corporation
Lowell, MA

- Recovery of acetone from a waste stream which was created by the regeneration of a carbon adsorption bed used to remove acetone vapor from the offgas in plastic filter products. (This particular waste stream was chosen as an example for operating cost estimation purposes. The cost estimate and the flow diagram are presented in Section IV.)

- The production of (penicillin) antibiotics results in the generation of large quantities of wastes containing butyl acetate. The waste is distilled and a portion of the butyl acetate can be recycled. The still bottoms, however, are hazardous wastes which contain 50% butyl acetate and 50% dissolved organics (fats and protein). These are disposed of by incineration.

- Waste motor oil from local service stations and from industrial locations can be re-refined to produce regenerated lube oil or fuel oil with the aid of distillation.

For a summary of waste form, types, and secondary potential byproduct wastes, see Tables 2, 3, and 4.

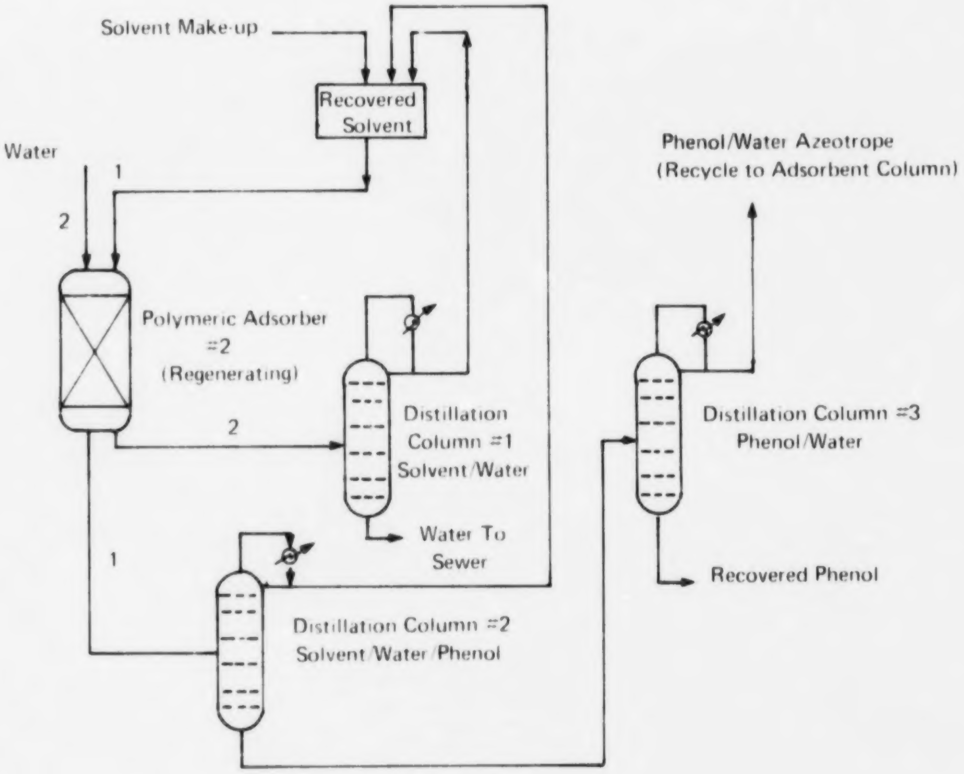

Solvent Make-up
Recovered Solvent
Water
1
2
Phenol/Water Azeotrope (Recycle to Adsorbent Column)
Polymeric Adsorber =2 (Regenerating)
2
Distillation Column =1 Solvent/Water
Distillation Column =3 Phenol/Water
Water To Sewer
1
Recovered Phenol
Distillation Column =2 Solvent/Water/Phenol

FIGURE 19 PHENOL RECOVERY APPARATUS

TABLE 2

WASTE FORMS THAT CAN BE DISTILLED

Waste Forms	Yes	No	Remarks
Aqueous Liquids	●		
Aqueous Vapors	●		
Organic Liquids	●		
Organic Vapors	●		
Gases	●		Cryogenic distillation
Slurries	●		After some form of pretreatment
Sludges	●		
Tars		●	
Solids		●	
Dry Powders		●	

TABLE 3

WASTE TYPES THAT CAN BE DISTILLED

Waste Types	Yes	No	Remarks
Inorganics		●	Possibly some exceptions, but these would not be relevant or practical to hazardous waste treatment or to its reclamation.
Organics:			
Plain Hydrocarbons	●		These are all general cases; there may be some exceptions to the rule.
Halogenated Hydrocarbons	●		
Amines	●		
Nitro Compounds		●	
Explosives		●	
Oxygenated Hydrocarbons	●		
Sulfur-containing Organics	●		
Phosphorus-containing Organics	●		
Lead containing Organics etc.	●		

TABLE 4

PHYSICAL FORMS AFTER DISTILLATION

Streams	(potential) Waste Form
Overhead	Aqueous Liquid or Vapor
	Non-Aqueous Liquid (condensed vapor)
Bottoms	Aquous Liquid
	Non-Aqueous Liquid
	Sludges
	Tars

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY AND ECONOMICS

The difficulty in separating the contents in the liquid to be distilled defines both the economics of distillation recovery and the energy requirements. The difficulty of separation is dependent on a number of things: the concentration of the feed, the degree of separation desired, the relative volatility of the constituents in the feed, the existence of contaminants, etc. For example, take the effects of different product purit[illegible]uirements for separation of a mixture of 50 mole % benzene in toluene at 25°C. Thermodynamic calculations for the minimum work required provide the following:

526 Btu/lb mole feed – both products 95 mole % pure
555 Btu/lb mole feed – both products 99 mole % pure
738 Btu/lb mole feed – both products 100 mole % pure

Capital investment is also affected since with higher product purity, larger size equipment is required and perhaps more sophisticated instrumentation. While exponents for equipment cost versus capacity are generally below 1.0 (e.g., glass-lined reactors, 0.41; shell and tube heat exchangers, 0.44 to 0.50; tanks, 0.6, etc.), for distillation columns the capacity-cost exponent is in excess of 1.0.* The incremental cost for incremental work of separation is thus escalating with successive increment.

For any binary distillation, there is an infinite number of design possibilities ranging between minimum reflex with an infinite number of stages on one hand, and minimum stages and total reflex on the other. From an economic standpoint, the optimum design is one that does the job at the lowest cost. Because both investment and operating costs are involved, a relationship must be presumed between them. Furthermore, since the particular relationship employed varies from company to company and from process to process, no single relationship between the two costs can be specified.

As the amount of liquid refluxed is increased, more energy is required for condensation and ultimate revaporization, thus escalating operating cost, but the number of stages is reduced, and this reduction lowers the investment required over the range of reflux ratios normally considered. (There is one exception to this rule. At higher-than-normally-used reflux ratios, the increasing reflux ratio increases the diameter of the column and the size of all auxiliaries, and reduces the number of required stages. Under these circumstances, investment costs would increase, with increasing reflux ratio.) Thus, the optimum design consists of balancing one cost against the other to obtain a minimum cost. At low reflux ratios, the calculated separation is sensitive to small operating changes and to relative volatility.

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*It is often necessary to estimate the cost of a piece of equipment of the same design configuration as another piece of equipment, but of a different capacity. This can be achieved with a fair amount of accuracy if the cost of the original equipment and its size (i.e., capacity) is known. According to the following equation:

Capacity of equipment A = Capacity of equipment B (cap. equip. A/cap. equip. B)$^{(\text{exponent})}$

Heat may be supplied to a distillation column by preheating the feed or by reboiling the bottom product. In general, preheating of feed should be minimized, reboiling heat maximized; since heat supplied to a preheater provides vapor only to the rectifying section, whereas reboiling heat is effective in the stripping section also. Sometimes, however, adding all the heat in the reboiler may make the column unbalanced with regard to vapor rates, the stripping vapor rates becoming larger than the rectifying rates; and then a larger diameter column may be required. In this latter case, preheating the feed would be a practical solution.

Other items which may affect the heat requirements for a column are whether or not the column is indoors or outdoors, what the prevalent ambient conditions are, and whether or not the column and the associated equipment are insulated.

Because of all of the variables which affect the capital investment and operating cost and the energy requirements for any particular distillation, there is no such thing as a typical cost for distillation on a unit product or on a unit feed basis. This becomes even more evident when all of the different organic liquids and the range of possible concentrations and the feed conditions (i.e., temperature, whether or not there are contaminants, etc.), are taken into consideration.

B. ENVIRONMENTAL IMPACTS

Waste treatment by distillation creates no air or liquid effluent problems that cannot be easily averted. Still bottoms may present a waste disposal problem, since they sometimes contain considerable quantities of tars and sludges which are usually incinerated. Vacuum distillation using steam or water eductors, yields volatile impurities in the condensed steam or water used to produce the vacuum. Disposal of this water is *always* a problem. Where disposal or treatment of this waste water is a major problem, mechanical vacuum pumps might be considered as an alternative to the eductor.

C. ECONOMIC ANALYSIS

To illustrate (but not typify) the economics of distillation, an economic analysis was performed on an "all-purpose" utility distillation system. This type of system is most likely to be installed where there is a high probability that many different types of organic liquid waste streams will be treated. Because the utility column is an all-purpose distillation column, it is not designed for optimization of operation with any one particular stream or flow rate in mind. As such, it has a high degree of flexibility. The utility column may be an adapted (used) piece of equipment, or it may have been specifically designed and fabricated to encompass operation on a range of common solvent-containing waste streams – at a projected average optimum of average operating conditions.

Cost evaluation here is based on a new equipment installation cost. This includes instrumentation, foundation installation, painting, piping, and engineering but excludes land value.

Estimates were based on January 1976 costs using a Chemical Engineering Plant Cost Index of 188.

The annualized costs of capital were established on the basis of a 10-year capital recovery factor with money borrowed at 10 percent interest. This method of annualizing capital costs has been widely used in pollution control cost estimating and is equivalent to off-the-books financing that might be obtained through the use of industrial pollution control bonds. The capital recovery factor for these cost estimates is 0.16274, i.e., the annual cost of capital is 16.274% of the total capital investment.

Operating labor costs were taken as $12.00/hr, which includes supervision and overhead charges. Annual maintenance (labor and material) was taken as a fraction of investment. Chemicals and utilities were charged at the unit prices noted.

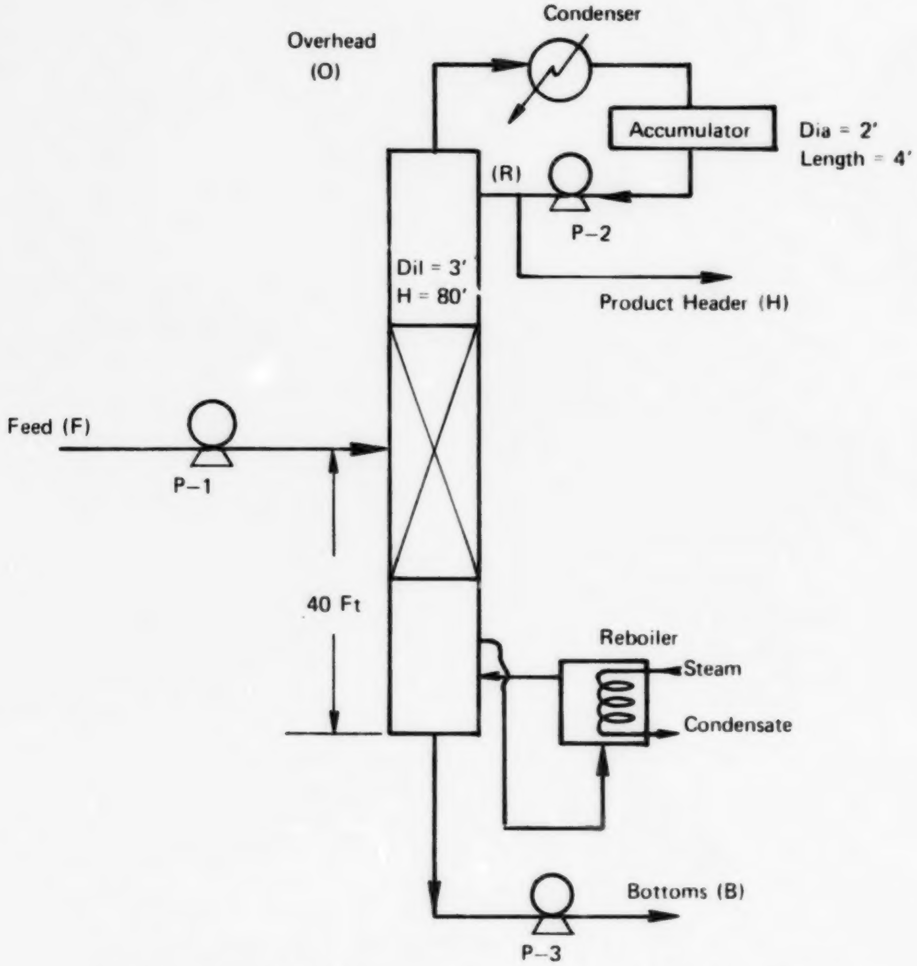
The equipment (see Figure 20) for economics evaluation is an actual utility system belonging to a solvent reclaimer. Some minor modifications to equipment sizing and arrangement were made to make the system more representative of one which would be installed (new) today. All equipment parameters are illustrated on the flow diagram.

A waste stream which was chosen for example is a 20% solution of acetone in water – a waste stream created by the regeneration of carbon absorption-bed, used to remove acetone vapor from the offgas in plastic filter production.

Cost estimates (see Table 5) are based on handling eight thousand pounds of waste per day. The column operates for 125 days per year at 8 hours per day – this represents 50% utility of the utility column. The other 50% of the on-stream operating time, the column is used to distill other waste streams. Thus, all capital-related charges are based on 50% of the total capital investment.

Total capital investment for new equipment is estimated to be $230,000. Of the total yearly operating costs for treatment of example waste stream, 64% is attributable to capital recovery charges. The total (fixed plus variable) cost of recovering a pound of acetone is 16.2¢. With a 70-80% byproduct credit for the quoted market value for acetone, the cost is 4.2¢/lb acetone.

As indicated previously, the solvent recovery cost is quite dependent on capital investment recovery charges. If a higher utility of the columns was charged to the same volume of acetone recovery, then the recovery cost would be proportionately higher, and vice versa. This would have a direct effect on the cost of acetone recovery.



Column: Diameter = 3 Ft
Height = 80 Ft
Packing = Berl Saddles (1–1/2" Stone)
Liquid Redistribution Plates
Every 4 Ft

Reboiler: 375 Sq Ft
Condenser: 100 Sq Ft
Pumps: Centrifugal (5 gpm Rating & 1/2 HP Motor)
Mat'l of Construction: S.S.

At Equilibrium:

Stream	Flow Rate lb/hr	Temp. (^{o}C)	Concentration (Wt. %) Acetone	Water
Feed (F)	1,000	21	20	90
Overheads (O)	812 lbs	59	98.5	1.5
Reflux (R)	609 lbs	59	98.5	1.5
Product Heads (H)	203 lbs	59	98.5	1.5
Bottoms (B)	797 lbs	100	0	1.5
				100

Notes: Column Operates Under Slight Positive Pressure. Reflux Ratio = 3.1

FIGURE 20 DISTILLATION OF 20% ACETONE IN WATER WASTE STREAM (ACTUAL SYSTEM)

TABLE 5

DISTILLATION – ESTIMATED OPERATING COSTS

Estimated operating costs for distillation of a 20% acetone-water waste stream with credit for acetone recovery.

Basis: 8,000 lbs of waste/day, 125 days/year* (8 hours/day)
50%* of utility column utilization (actual system)

Capital Investment: $230,000

	Annual Quantity	Cost per Unit	Annual Cost	
Variable Costs:				
• Operating Labor	375 hrs/yr**	$12/hr	$ 4,500	
• Utilities:				
– Cooling Water	535,000 gal/yr	$0.03/1,000 gal	16	
– Makeup Water	6,000 gal/yr	$0.40/1,000 gal	2	
– Steam (20 lbs)	1,000 MM Btu/yr	$4.00/MM Btu	4,000	
– Electricity	290 kWh/yr	$0.02/kWh	6	
• Maintenance (3% Inv.)*			3,450	
Total Variable Costs				$12,000
Fixed Costs:				
• Taxes & Insurance (2% Inv.)*			2,300	
• Capital Recovery (10 yrs. @ 10%)*			18,000	
Total Fixed Costs				20,000
Total Cost/Year				33,000
Total Cost/Lb Acetone Recovered			$0.162/lb	
• Chemical (acetone) credit	203,000 lb/yr	$0.120/lb credit		(24,360)
Net Cost/Lb Acetone Recovered (incl. credit)			$0.042/lb	

*Utility column is used for other waste streams. All charges for capital or related to capital are based on 50% utility.

**Actual reported figures. This distillation system was continuously operated in an area where other solvent reclamation projects were operating, thus requiring only part-time attendance. This figure could be higher for other feed materials or waste disposal companies.

It may be more economical for those who generate relatively small volumes of solvent effluents to pay a contractor to haul the waste stream away; have him recover the acetone; and then buy it back. One contractor visited by ADL staff performs just this service for a client. Total cost to the *client* for recovery of acetone is about *15¢/lb* of recovered acetone, which is approximately 2-3¢/lb less than quoted market value for virgin acetone, a saving of 13-20% over market value. The solvent reclaimer, on the other hand, makes about a 10% profit (above overhead), since he normally has a much lower capital recovery charge than would the manufacturer. This is because:

1) His capital investment may be lower – for used equipment, or old equipment which has already been written off, or

2) He probably can make better overall utility of his equipment, thus imposing lower utility capital cost application for each particular waste stream handled. In this case, with second-hand equipment, the fixed cost as shown in Table 5 would be reduced to about $14,000/yr, for a total recovery cost of $26,000/yr, or 12.8¢/lb acetone.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Currently, distillation is being used for the recovery of liquid organics from liquid waste streams.

Listed below are the criteria for waste recovery via distillation.

- Distillation can:
  - Separate, segregate, or purify to high quality standards. This could mean that the recovered solvent may be directly recyclable or salable.
- Distillation cannot:
  - Deal practicably with waste azeotropes unless they are consistently reliable in composition and available in large volumes over extended periods of time.
  - Handle feeds having high quantities of solids tars, or feeds that tend to polymerize without suffering severe consequences unless the streams can be pretreated to reduce or remove these materials.
- Advantages of distillation:
  - It does not destroy but recovers.
  - Product purity can be attained to any desired level, at a cost.
- Disadvantages of distillation:
  - Equipment and auxiliaries are usually comparatively large. They can have heights up to 200 ft and cover large land areas.
  - The equipment is expensive, and capital recovery charges usually constitute the major portion of solvent recovery cost.
  - Recovery is energy-intensive and is a close second to capital recovery charges. Energy requirements are nominally 250-1200 Btu/lb of feed.
  - Its application to feed is limited in that it will handle only liquid solutions which are relatively "clean."
  - Equipment is often complex and requires operation by highly skilled personnel.

- Still bottoms sometimes contain tars and sludges which must be disposed of in landfill or by incineration.

Distillation equipment is expensive, and recovery by distillation is energy-intensive. To some degree, design of the equipment (as outlined in Section II) can balance the cost of the equipment against the amount of energy required for distillation. As the energy situation worsens, the balance will tend to favor high equipment cost. But both costs will increase, thus increasing the cost of chemical recovery by distillation. But with the increased cost of energy, the cost of the production of virgin organic chemicals should also increase. This increased cost of organic chemicals will provide increased byproduct credit which will have a positive effect on reduction of the cost of solvent recovery by distillation.

In addition, air and water pollution regulations have either directly or indirectly created more waste streams to which distillation is applicable. Furthermore, there are no air or liquid effluent problems with distillation that cannot be averted. Still bottoms, however, may present a waste disposal problem, since they sometimes contain considerable quantities of tars and sludges.

Distillation is expensive and energy-intensive, but with increases in byproduct credits, it can sometimes compete with processes having a much lower capital recovery charge. With some modifications in the operation of older equipment and by designing newer units with energy conservation in mind, there can be a small (but significant) savings in the energy needed to distill a particular organic waste. When distillation is directly competitive on an economic and an energy basis, distillation is preferred to disposal because of its conservation aspects.

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B. PEOPLE AND ORGANIZATIONS EXPERIENCED IN THE FIELD

1. Mr. J. Ward – CPS Chemical Co.
   Old Bridge, NJ

2. Mr. R. West – Chempro
   Seattle, WA

3. Mr. N.B. Hjersted – Conservation Chemical
   Kansas City, MO

4. Mr. E.R. Shuster – Chem-Trol Pollution Services, Inc.

5. Dr. J. Miserlis – Silresim Chemical Corp.
   Lowell, MA.

ELECTRODIALYSIS

Prepared by

James D. Birkett

I. CONCLUSIONS AND RECOMMENDATIONS

Electrodialysis is generally applicable to the separation of an aqueous salt stream into dilute and concentrated streams. It is most useful over the range 200-5000 ppm with overall costs of operation usually ranging from $1 to $5 per thousand gallons. It does not affect undissociated organic species.

Electrodialysis is not available as standard "turnkey" equipment for pollution control, and its design and operation may require more skill and care than that of other systems with which it may compete. It will probably continue as a viable process in those applications for which it is especially suitable but it does not appear to have general utility as a waste treatment tool. Its most likely areas of application in the industrial waste treatment field will likely be for recycle/reuse of recovered product.

II. PROCESS DESCRIPTION

A. UNDERLYING PRINCIPLES

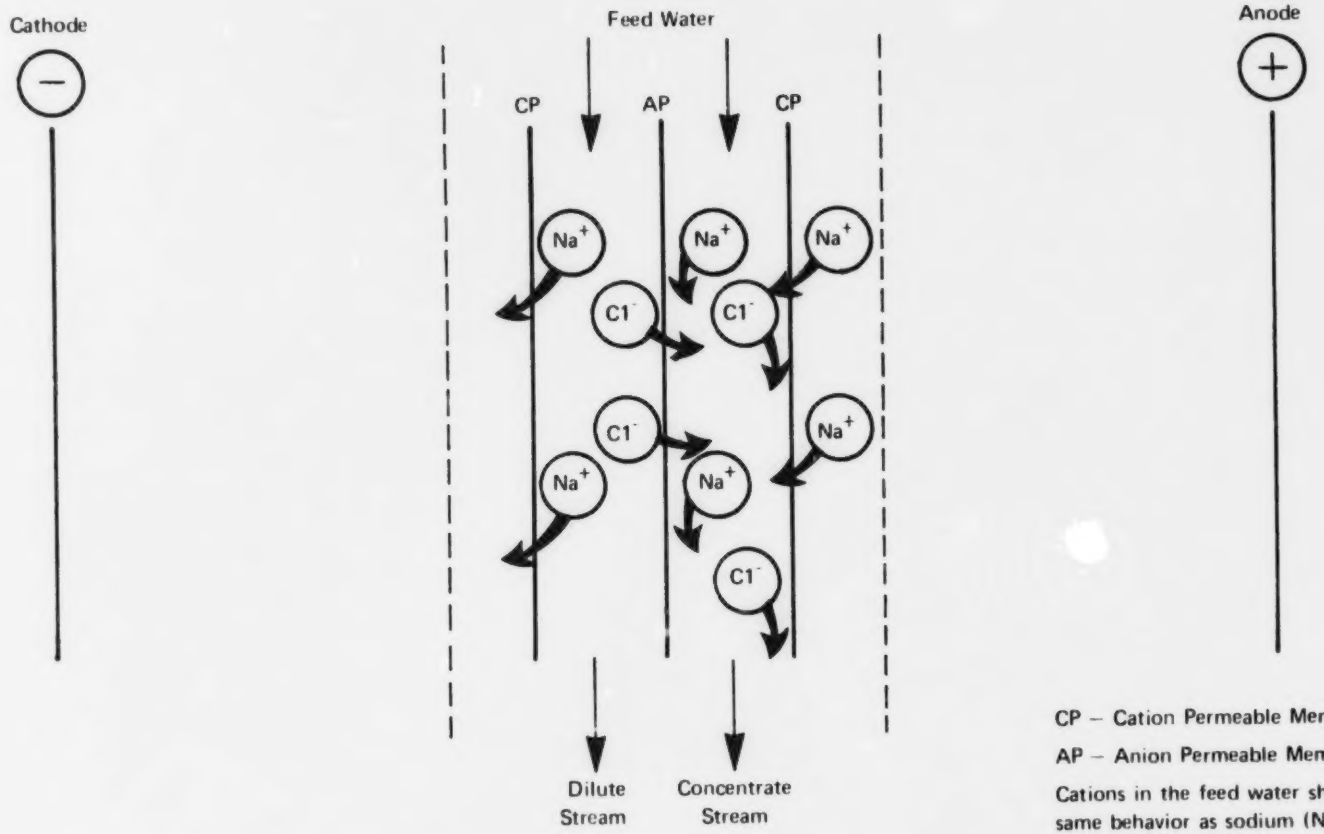
The general function of electrodialysis (ED) is the separation of an aqueous stream under the action of an electric field into two streams: an enriched stream (more concentrated in electrolyte than the original), and a depleted stream. Success of the process depends on special synthetic membranes, usually based on ion exchange resins, which are permeable only to a single charge type of ion. Cation exchange membranes permit passage only of positive ions under the influence of the electric field, while anion exchange membranes permit passage only of the negatively charged ions.

The feed water passes through compartments formed by the spaces between alternating cation-permeable and anion-permeable membranes held in a stack. At each end of the stack is an electrode that has the same area as the membranes. A dc potential applied across the stack causes the positive and negative ions to migrate in opposite directions. Because of the semipermeability of the membranes, a given ion will either migrate to the adjacent compartment or be confined to its original compartment, depending on whether or not the first membrane it encounters is permeable to it. As a result, salts are concentrated or diluted in alternate compartments. The process is shown diagrammatically in Figure 1.

To achieve high throughput, electrodialysis cells in practice are made very thin and assembled in stacks of cells in series. Each stack often consists of more than 100 cells. Feed material is first filtered to remove suspended particulate matter which could clog the system or foul the membrane and, if required, is given a pretreatment to remove oxidizing materials and ferrous or manganous ions which would damage the membranes. Very high organic levels may also lead to membrane fouling. The catholyte stream is commonly acidified to offset the increase in pH which would normally occur within the cell, and an antiscaling additive may be required as well. An operating plant usually contains many recirculation, feedback and control loops and pumps to optimize the concentrations and pH's at different points and thus maximize the overall efficiency. Although a certain amount of water transfer (electrosmosis) does occur, the process can be categorized with ion exchange, solvent extraction, or adsorbent processes as one in which solutes are removed from the solvent, rather than with distillation, freezing, or reverse osmosis in which the solvent is transported.

All ionized species are not removed in proportion to their concentration because of different mobilities and equilibrium concentrations within the membrane. Therefore, a solution partially deionized or concentrated by electrodialysis may contain significantly different proportions of ionized species than the original feed.

Many colloids and polyanions have a net negative charge. For this reason they may collect upon or foul anion exchange membranes because of their positively charged functional groups. This problem may be avoided to some extent using an electrodialysis cell



CP – Cation Permeable Membrane

AP – Anion Permeable Membrane

Cations in the feed water show the same behavior as sodium (Na^+), and anions the same behavior as chloride ($C1^-$).

FIGURE 1 DIAGRAMMATIC REPRESENTATION OF ELECTRODIALYSIS

that consists of alternating cation and "neutral" membranes. Such systems utilizing a porous "neutral" membrane to avoid convective flow or mixing, frequently perform very well from a separation standpoint although they are not common commercially because of their higher electrical power requirements.

Perhaps the most important difference between electrodialysis and many other separation processes is that it requires oxidation and reduction reactions to take place at the electrode surfaces. At the cathode, frequently stainless steel, the reduction of water to form gaseous hydrogen is the most common reaction:

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2\,OH^-$$

However metal ions can and frequently do plate out as well. The increase in hydroxyl ion (OH^-) concentration frequently leads to scaling or the precipitation of insoluble species. An easily reduced organic species present at the electrode surface could be reduced as well.

At the anode there also are very interesting sets of possible oxidation reactions. In caustic solutions, or those low in chloride, the predominating reaction is:

$$H_2O - 2e^- \longrightarrow 1/2\,O_2\uparrow + 2H^+$$

In chlorine-containing solutions, however, the following reaction may take place:

$$Cl^- - e^- \longrightarrow 1/2\,Cl_2\uparrow \quad \text{or}$$

$$Cl^- + 2\,OH^- - 2e^- \longrightarrow OCl^- + H_2O$$

Thus there may be some local problem with air contamination or with chlorination of organic species. (However, these reactions may also be utilized for the sterilization of the anode stream.) Anodes are made of non-oxidizable conductive materials such as platinitized titanium.

As the purity of the product water increases, its electrolytic conductivity decreases. This higher resistance makes it increasingly less efficient to remove the remaining salt. In addition each stack of cells in series reduces the salt concentrations by a more or less fixed percentage. Thus the capital equipment (but not the energy) necessary to remove 250 mg/l salt from a 500-mg/l stream is comparable to that required to remove 2500 mg/l from a 5000-mg/l stream. For these reasons, most large plants today do not produce a dilute stream of much less than 500 mg/l and very few operate as low as 200 mg/l.

B. OPERATING CHARACTERISTICS

Generally the system works best on acidic streams containing a single principle metal ion (such as acid nickel baths). At alkaline pH's membrane life may diminish, but the system has been reported useable up to pH 14 under special circumstances. Mixed metals may not be concentrated in the same ratio as that in the feed, leading to problems in recycle. In addition, although a sodium and copper cyanide stream may perform as expected under electrodialysis, the presence of zinc (a common occurrence, especially in brass plating) can foul the anion membrane by the $(ZnCl)^-$ ion and partially convert that membrane to the cation form, with significant loss in system performance.

If strongly alkaline, the feed streams are generally neutralized or rendered slightly acidic to prevent degradation of the anion membrane, which usually contains quaternary ammonium groups. Iron and manganese in the feed water also degrade most common membranes and must be removed if their total concentration in the feed water is greater than about 0.3 mg/l.

Calcium sulfate scale can also accumulate if the calcium concentration in the concentrated stream is allowed to go above about 400 mg/l. Addition of a sequestering agent to the feed permits operation to a higher calcium concentration, but generally not above 900 mg/l. For this reason, the brine rarely constitutes less than 10 to 15% of the feed water volume (a concentration factor of 6-10).

Because the process depends on electrolytic conductance through the various liquid streams it is rarely practical to produce product water of less than about 250 ppm total dissolved solids. For the same reason, it is often desirable to operate an electrodialysis system at a slightly elevated temperature. As a rule of thumb a temperature increase of 17°C reduces the power consumption by 1%.

Membrane life, although dependent upon service conditions, is frequently five years. Other components are generally long lived, because the system, although somewhat corrosive perhaps, operates at modest or ambient temperatures and pressures and abrasives and particulates normally will have been removed from the feed water.

III. APPLICATIONS TO DATE

A. HISTORY OF USE

Early development work in electrodialysis was carried out at Ionics, Inc., and Rohm & Haas in the early 1950's. The Netherlands Government research organization, T.N.O., also began work on the process about the same time. Rohm & Haas, drawing upon its background in ion exchange resins, prepared membranes by pressing very fine resin particles into an open polyethylene backing. By contrast, Ionics started with cross-linked polystyrene sheets to which the functional exchange groups were subsequently attached. After about five years the Ionics material established dominance, largely because of the lower resistance of that membrane, and Rohm and Haas retired from the field. However, anticipated markets for the process, largely in desalination of sea water, lured new companies into the area in the late 1950's and early 1960's. The National Aluminate Company, aided by the ion exchange technology of the Dow Chemical Company entered the field as Permutit through its Ionac subsidiary. American Machine and Foundry (AMF) began offering units with some technology licensed from T.N.O. Aqua-Chem, Inc., in turn began the production of electrodialysis units utilizing AMF membranes. The situation simplified somewhat in 1964 when AMF was found in infringement of Ionics patents and withdrew as a major source.

Perhaps the most aggressive foreign activity has been that by Asahi Chemical Industries in Japan. Asahi initially focussed on the concentration of sea water for salt production but more recently has expanded into water and waste treatment. In April 1976, Dow Chemical Company announced that it would market the Asahi system in the United States. The work initiated by T.N.O. is being utilized in Europe by Boby, Ltd., and Bronswerk, N.V.

The Office of Saline Water, U.S. Department of the Interior, was a major source of research support during the early days of electrolysis. The largest number of (ED) installations is probably in the production of potable (~ 250 ppm TDS) water from brackish well or river water (2000-5000 ppm). Hundreds of such units, ranging in size to more than one million gpd are in use throughout the world. Some of these units have been in service for as long as 15 years (although membranes have been replaced).

B. PRINCIPAL CURRENT APPLICATIONS

Industrial applications are widespread but varied and include the use of the process to remove the mineral constituents or contaminants from process streams that contain large amounts of organic products, e.g., de-ashing of sugars, washing of photographic emulsions, and demineralization of whey. It frequently is used in the production of potable water from brackish waters, for the desalting of food products such as whey, and in the chemical industry for a variety of solution enrichment or depletion purposes.

Pilot operations have been carried out on the desalting of sewage plant effluent, sulfite-liquor recovery, acid mine drainage treatment, the desalting of cooling tower waters, and numerous other industrial applications. Treatment of plating wastes and rinses has been studied and piloted with encouraging but generally modest results. Recent work at General Motors (still unpublished) suggests use of the process to salvage chromium wastes from chromic plating rinses.

At least two facilities have installed electrodialysis units to treat the hydrogen fluoride and ammonium fluoride effluents from glass and quartz etching facilities. Starting with a feed stream that contains 400-500 ppm fluorides, it is possible to produce a dischargeable dilute stream and a low-volume concentrate stream which may be recycled or economically treated.

An interesting example of the use of electrodialysis in series with reverse osmosis for the treatment of a concentrated salt (NaCl) stream is outlined in Figure 2. Such a system is presently in the pilot plant stage and although cost data are not yet available, it shows how a system utilizing more than one type of process may be arranged. Here electrodialysis is chosen for the salt-rich end of the system where it can operate at high current efficiency.

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Laboratory and pilot plant work is being carried out on the application of electrodialysis to other waste streams but no projects of special interest or impending commercialization have been identified.

C. POTENTIAL APPLICATIONS TO WASTE TREATMENT

Electrodialysis is of possible applicability whenever it is desired to separate an aqueous waste stream containing 1000-5000 ppm inorganic salts into a dilute stream that contains 100-500 ppm salt and a concentrated stream that contains up to about 10,000 ppm salt. For this reason, electrodialysis by itself cannot be considered a solution to a waste problem but must be tied into further concentration or reuse schemes.

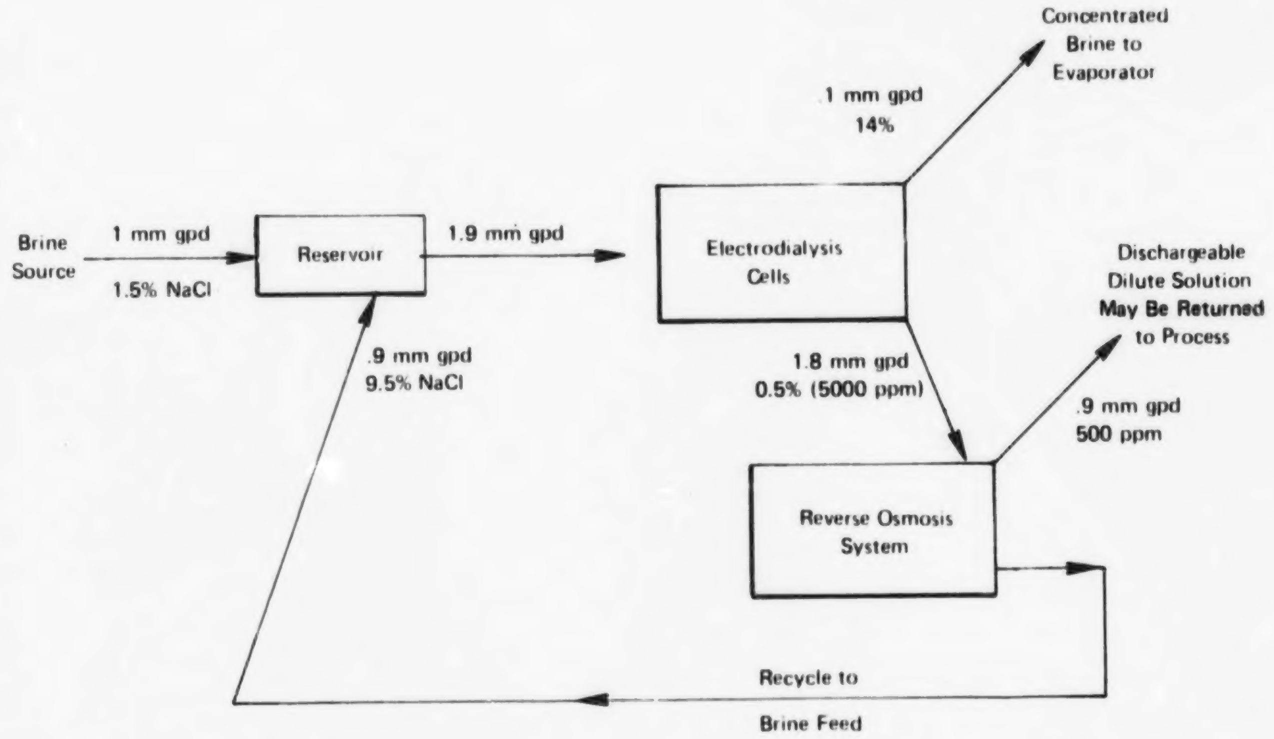

FIGURE 2 ELECTRODIALYSIS COMBINED WITH REVERSE OSMOSIS

IV. ENERGY, ENVIRONMENTAL ISSUES, AND ECONOMICS

A. ENERGY REQUIREMENTS

Electrical requirements for electrodialysis vary but a useful rule of thumb in conventional operating systems is about 5 kWh of energy for each 1000-ppm reduction of salt in each 1000 gallons of purified product water. (Thus, reducing a stream from 3500 ppm to 500 ppm would require 15 kWh/1000 gallons.) In addition, up to 3 kWh may be required to pump each 1000 gallons of products. There is no thermal energy input requirement.

B. ENVIRONMENTAL IMPACTS

As an electrodialysis plant produces two product streams, one concentrated and one dilute in the original contaminants; these must be either recycled, sold, or disposed of in some other manner.

Electrodialysis may cause some local air pollution, because both H_2 and a Cl_2O_2 mix may be generated at the electrode surfaces. These represent a hazard if permitted to collect in an enclosed space; therefore, they generally are vented to the outside and allowed to escape into the atmosphere.

C. ECONOMIC ANALYSIS

Unlike some processes, e.g., reverse osmosis, the capital costs of electrodialysis are modest, 20-25% of the total cost of water treatment. However, both capital and direct operating costs are very dependent not only on the volume of water to be treated, but also on the amount of salts to be removed. This is best visualized by considering an electrolysis plant as a number of cell stacks in parallel and series array. Each stack module is capable of processing a given volume of water per day and reducing its salt content by a fairly fixed percentage (usually 50-70%). Thus twice as much throughput requires twice as many stacks in parallel.

Of perhaps more significance is the manner in which the number of series-connected stacks increases as water purity is increased. If a single stack under certain feed conditions will reduce total dissolved solids by 60%, a 10,000-ppm feed may be reduced to 4,000 ppm by one stack, to 1600 ppm by two, to 640 by three, and to 256 ppm by four stacks. Thus the capital cost to remove the first 8400 ppm (10,000-1,600) is approximately the same as that to remove the last 1344 ppm (1600-256).

While total water production costs of less than $0.50 per thousand gallons are frequently reported for electrodialysis, such a price is generally for a salt reduction of the order of 2000 ppm to 500 ppm and for plants operating at a level of 1 million gal/day or more. For higher concentrations of feed and purer product water, prices between $0.50 and $1.00 are common and may be higher depending on preprocessing units, prices of electrical energy, etc. Smaller facilities are more expensive in terms of cost per volume throughput but may receive significant credits for reclaimed material.

As an example, consider as a model an electrodialysis system designed to treat the first and second noncascaded rinse tanks from an acid nickel plating line. (See Figure 3.) It is desirable to maintain the first rinse tank at about 3.5 g/l nickel and the second rinse at about 0.2 g/l nickel. Drag-out by parts from the plating tank (90 g/l nickel) is 400 g/hr nickel. Drag-out from rinse 1 to rinse 2 is about 9 g/hr. A system such as that shown will return 373 g/hr of nickel to the plating tank at nearly plating strength and will reduce the nickel losses considerably.

Table 1 gives cost estimates for such a plant. If the total costs are converted into unit costs, a figure of \$6.10/Kgal is developed (based on total throughput of both units). However, this figure must be adjusted downwards by the potential credits which develop from saving 373 g of nickel per hour or 2.1 lb/1000 gallons of water treated. Non-ionic constituents, such as the organic brighteners generally added to nickel plating tanks, will not be retained by this system and will have to be replenished.

A second example is the system proposed by Jordan et al.[14] for sidestream treatment of cooling tower water (Figure 4). The cooling tower has make-up requirements of 2,000 gallons per minute (gpm). The make-up water contains 0.1% salts and thus adds about 12 tons of salt per day to the system (assuming water loss solely by evaporation).

The cooling tower recirculates 100,000 gpm at a design concentration of 1% salts. An electrodialysis unit may be designed to operate in a 500-gpm sidestream loop, yielding a concentrate of 13 gpm of 15% brine and a dilute stream to be fed back to the system. The concentrated brine has a content of 12 tons per day of salts, equal to that introduced in the make-up water. This brine may then be disposed of by ponding or some other acceptable technique.

Capital cost for such a system could be of the order of \$450,000 (63 cents per gpd capacity). Energy requirements at these high concentrations could approach 25 kWhr/1000 gallons, or 18,000 kWhr/day. Membrane replacement would be of the order of \$7,000 per year. Labor will be (at a maximum) one operator per shift plus a supervisor four hours per day.

If it is assumed that there is no cost for land acquisition and site preparation, and that the feed stream does not require pretreatment due to high alkalinity or the presence of species such as iron or manganese, the approximate costs shown in Table 2 may be generated. These costs should not be considered typical but merely an illustration of the contributions of various economic factors. For example, the cost of electricity is nearly one half of all direct variable costs in this case, due to the large quantities of salts removed. For a more dilute system, costs would be considerably less.

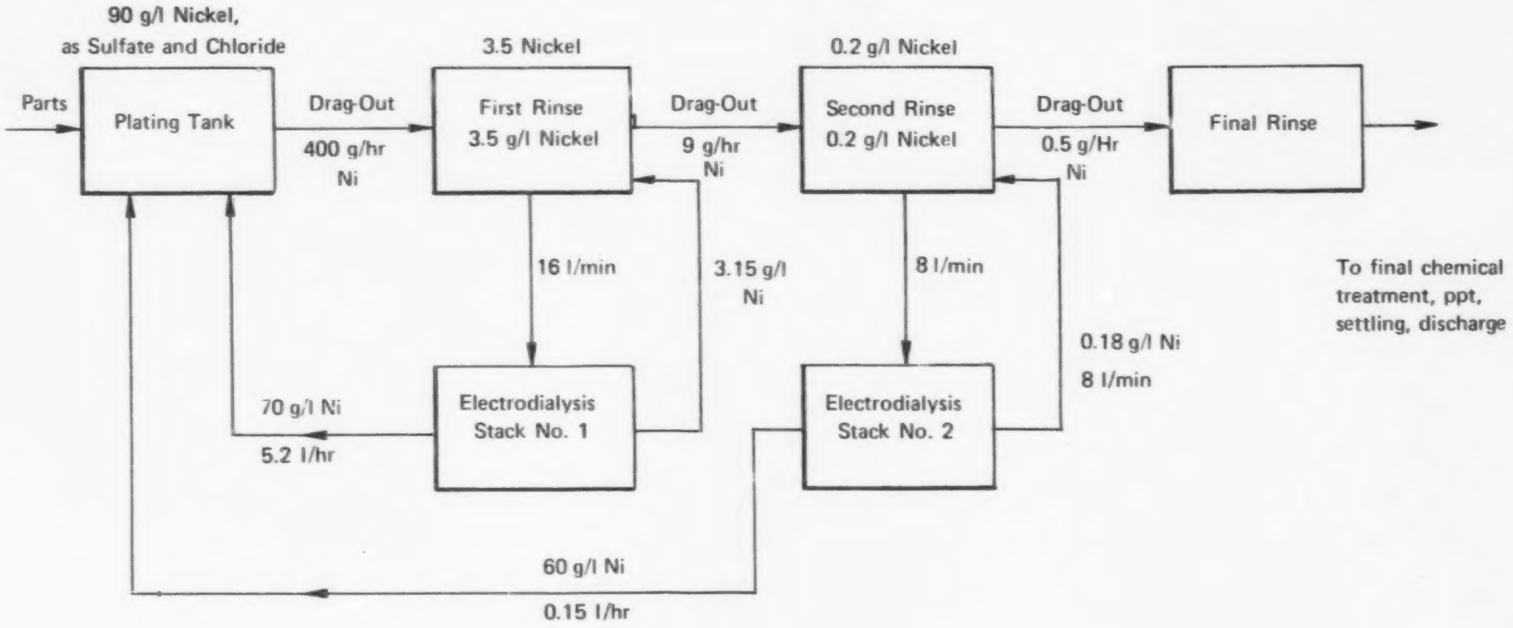

FIGURE 3 ELECTRODIALYSIS RECLAMATION OF $NiSO_4$ FROM NON-CASCADED RINSES OF NICKEL PLATING LINE

TABLE 1

ESTIMATED OPERATING COST FOR ELECTRODIALYSIS

Basis: Reclamation of $NiSO_4$ from noncascaded rinses of nickel plating line. Two units, 330 days/year operation

Capital Investment: $24,000

	Annual Quantity	Cost Per Unit Quantity	Annual Cost ($)
Variable Costs			
Operating Labor	1050 MH	$12/hr	12,600
Chemicals			100
Utilities			
Electricity	35,700 kWh	$0.02 kWh	700
Membrane Replacement			1,400
Total Utilities			
Maintenance as 4% Inv			960
Total Variable Costs			15,800 (rounded)
Fixed Cost			
Taxes & Insurance of 2% Inv			480
Capital Recovery (10 yrs. at 10%)			4,000
Total Fixed Costs			4,480
Total Annual Costs			20,300
Cost per 1000 gal Throughput			$6.10
Cost per kg of Ni Reclaimed			$6.90

Source: Arthur D. Little, Inc. estimates.

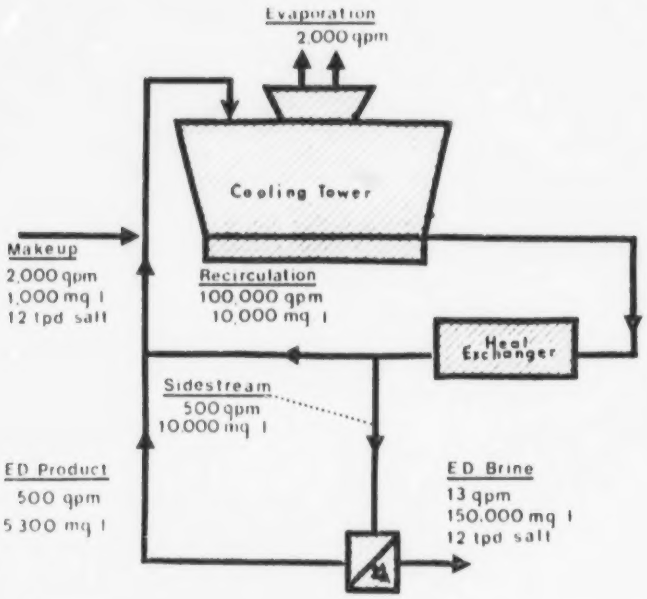

FIGURE 4 HYPOTHETICAL MASS BALANCE FOR A COOLING TOWER CIRCUIT WITH SIDE STREAM ELECTRODIALYSIS

TABLE 2

ESTIMATED OPERATING COSTS FOR ELECTRODIALYSIS

Basis: Side stream electrodialysis of cooling tower water. Single stage, 720,000 gpd, 300 days per year operation.

Capital Investment: $450,000

	Annual Quantity	Cost per Unit Quantity	Annual Annual Cost
Variable Costs			
Operating Labor	9,240	$12/hr	$111,000
Chemicals			10,000
Membrane Replacement			7,000
Utilities			
Electricity	6,000,000 kWhr.	$0.02/kWhr.	119,000
Maintenance			
As 4$ Investment			18,000
Total Variable Costs			$265,000
Fixed Costs			
Capital Recovery (10 yrs at 10%)			$ 84,000
Taxes and Insurance at 2% of Investment			9,000
Total Fixed Costs			$ 93,000
Total Costs		**$1.51/1000 gal.**	**$358,000**

Source: Arthur D. Little, Inc., estimates.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

At present there is no center of aggressive promotion of electrodialysis. A number of small firms are engaged in engineering work on a modest scale but the lack of significant identifiable markets has kept the number of entrants low. Should such markets appear, however, the technology would be within the reach of numerous companies in the chemical and waste treatment field and it would seem reasonable that the number and position of suppliers could change considerably.

Electrodialysis profits by the fact that it is a mature technology with well-known performance characteristics and prices and therefore can be easily evaluated as a potential component of any multi-process treatment being considered. However, its success may be determined to a large extent by whether it can be made sufficiently reliable and attention-free to be offered as a "black box" treatment package.

Despite its limitations regarding concentration range and types of solutes transferred, electrodialysis will continue to find a modest number of industrial applications, especially in the recycle/reuse area.

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B. PEOPLE AND ORGANIZATION EXPERIENCED IN THE FIELD

Asahi Chemical Industries (Japan)
Dow Chemical Company
Ionics, Inc.
National Aluminate Company
Office of Saline Water, U.S. Department of the Interior
T.N.O. Aqua-Chem., Inc.

ELECTROLYSIS

Prepared by

James D. Birkett

I. CONCLUSIONS AND RECOMMENDATIONS

Electrolytic processes, while limited in applications to waste streams, may be considered for reclaiming heavy metals, including toxic metals from concentrated aqueous solution and in polishing dilute metal streams. It is not generally useful in treating dissolved organics, organic waste streams or viscous and tarry liquids. Destruction of cyanides and the treatment of chrome wastes is the subject of research and has undergone encouraging pilot testing but as yet there is no significant commercial use.

II. PROCESS DESCRIPTION

A. UNDERLYING PRINCIPLES

The terms electrolysis or electrolyte reaction are applied to those reactions of oxidation or reduction which take place at the surface of conductive electrodes immersed in a chemical medium, under the influence of an applied potential. At the negative electrode, or cathode, the reactions may include the reduction of a metal ion to the metal itself, $M^+ + e' \rightarrow M$, or, in aqueous media, the reduction of the hydrogen ion or water to hydrogen gas

$$2H^+ + 2e' \longrightarrow H_2 \uparrow$$

or

$$2H_2O + 2e' \longrightarrow H_2 \uparrow + 2OH'$$

The potential at which each such reaction takes place at 25°C and with all reactants and products at unit activity is termed E° for that reaction (E° measured versus the normal hydrogen electrode as a reference point). For conditions in which all reactants and products are not at unit activity, the required potential is given by the Nearnst equation.

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

in which n is the number of electrons required in the reduction (or oxidation) step and Q is the product of activities of product materials divided by the activities of the reactants.

Oxidation reactions, including

$$2Cl' \longrightarrow Cl_2 \uparrow + 2e'$$

or

$$2H_2O \longrightarrow O_2 \uparrow + 4H^+ + 4e'$$

or

$$4OH' \longrightarrow 2H_2O + 4e' + O_2 \uparrow$$

may be described likewise.

Values of E° for most oxidation and reduction reactions in aqueous solution range from about +3 to -2 volts but many cannot be utilized due to the low potential, 1.23v, at which water electrolyzes into hydrogen and oxygen.

(Actually, under operating conditions, an aqueous system will usually function at applied potential a few tenths of a volt higher due to a phenomenon called overvoltage. This is characteristic of gas evolution at electrodes whereby, depending on the gas and the electrode material, slightly higher potentials than those predicted by theory are required, due to surface adsorptive characteristics.)

From the Nearnst equation, it is apparent that for an aqueous solution containing several species at various concentrations, the potentials of the various possible electrode reactions may be sufficiently close in value that several reactions could take place at a single electrode. As a result, in practical situations it is common to speak of the efficiency of an electrode reaction, i.e., that percentage of the current that results in the desired reaction rather than other possible side reactions.* Obviously for maximum economy, high current efficiency is desirable; values from 10% to virtually 100% may be found in the electroplating industry.

The applied voltage necessary to promote a desired electrode reaction is not only dependent upon the theoretical cell voltages (and overvoltages) mentioned above, but also contains corrections for concentration changes in the neighborhood of the electrodes and simple IR losses due to the electrolytic resistance of the solution itself. For this reason, commercial electrochemical cells generally contain some form of stirring to reduce concentration effects and narrow electrode spacing to minimize resistance.

As a further note, it should be recognized that in conventional low voltage electrolysis, transport of reactants and products to and from electrode surfaces is limited by ordinary diffusion processes under the concentration gradients developed by the electrode reactions. This is in contrast to electrophoresis in which transport takes place as a result of the influence of the high voltage electric field upon charged particles.

Table I shows the calculated values of the maximum diffusion-limited current for copper deposition at various levels of copper concentration. At current densities approaching this maximum, the current efficiency falls off significantly.

Common to all electrolytic processes, including these mentioned above, is the problem of maintenance of a high performance electrode surface. Anodes especially are prone to attack and may become so oxidized that they are no longer useful. This may be especially true for carbon anodes where significant wastage may change the dimensional tolerance of the electrolytic cell. Obviously anode consumption and replacement should be treated among the economic factors in evaluating such a system.

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*Under conditions of 100% current efficiency one gram-equivalent weight of a reactant is consumed (or product generated) by 96,500 ampere-seconds of current, an amount known as one coulomb.

TABLE 1

DIFFUSION CURRENT MAXIMA FOR COPPER AT 25°

Cu^{++} Concentration		Maximum Current Density	Maximum Copper Deposition
Moles/1	ppm (as Cu)	A/cm^2	$g/cm^2/hr$
10^{-1}	6300.00	1.4×10^{-2}	17.00 mg
10^{-3}	63.00	1.4×10^{-4}	.17 mg
10^{-5}	0.63	1.4×10^{-6}	.0017 mg

Source: Ref. 7

While dimensional changes in the cathode due to metal deposition are more predictable, other more subtle changes may take place. For example, a cathode substrate chosen to have a high overvoltage for hydrogen evaluation in order to permit operation at higher voltages and thus higher currents will, upon being plated with metal "M" begin to exhibit the characteristics of an "M" electrode. Cathode efficiency may thus fall.

The most common, least predictable, and most difficult to control form of electrode deterioration is that generally referred to as fouling. By this is meant the accumulation at the electrode surface of a coating of insoluble salts, oxides, organic materials, and biological films which interpose a high resistance barrier to the desired electrolytic barrier. For example, an inefficient cathode evolving hydrogen according to the equation

$$2H_2O + 2e \longrightarrow H_2 \uparrow + 2OH$$

is also developing a region of high pH which may cause precipitation of species which are in solution at the pH of the feed. Likewise organic films or slimes may deposit. These may be slowly accumulated and may be present in the feed only in minute quantities. Also variations in feed may be enough to push the chemistry at an electrode surface from a nominally non-fouling condition to a fouling one.

III. APPLICATIONS TO DATE

A. APPLICATIONS IN INDUSTRY

Electrolysis, including electroplating and anodizing, is part of industrial chemistry today and has been such for many years. A few examples will indicate its breadth of use.

1. Chlorine-Caustic Production

The bulk of the U.S. production of chlorine, amounting to many millions of tons per year, is achieved through the electrolysis of concentrated aqueous solutions of sodium chloride. In one type of system, chlorine and hydrogen are evolved at inert* anodes and cathodes, respectively, to give the overall cell reaction

$$2NaCl + 2H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$$

The concentrated caustic formed in the cathode compartment by the half cell reaction

$$2H_2O + 2e' \longrightarrow H_2 + 2OH'$$

is kept from mixing with the bulk of the brine electrolyte by means of a porous diaphragm, generally composed of asbestos fibers.

In an alternative method for chlorine/caustic production, the cathode may consist of a bed of metallic mercury which makes possible the reaction

$$2NaCl \longrightarrow Cl_2 + 2Na \text{ (amalgam)}$$

The amalgam is subsequently removed and reacted with pure water to give NaOH free of chloride contamination. (This system, once popular, has been largely displaced by the aforementioned diaphragm cell, not only for economic reasons, but also because of the environmental problems associated with such large-scale use of mercury.)

2. Metal Refining

Many commercial metals are routinely refined by electrolytic processes in order to remove impurities. Bismuth, copper, gold, indium, lead, nickel, silver and tin are generally treated in this manner. In practice, the anode is a bar of the impure metal and the cathode a plate of pure metal or an inert conductor. The electrolyte may be a strongly acidic, alkaline, or neutral bath, depending upon the metal being refined and the nature of the impurities. It is frequently chosen at or near the concentration of maximum electrolytic conductivity in order to minimize power losses.

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*In the past, these have been made of graphite but new materials less prone to oxidation have recently been introduced.

3. Electrowinning

In contrast to the electrorefining of impure metals, electrowinning may be employed to obtain metals from electrolytes derived from the primary metal ores. Such a process is frequently used to obtain copper, zinc, cadmium, cobalt, gallium, and other metals. For example, cadmium is generally present in significant quantities in the sludges and residues from zinc refining. The source materials are dissolved in sulfuric acid, pretreated as necessary to remove copper and certain other impurities, and the cadmium plated out onto aluminum cathodes. Oxygen is generated at the anodes which is usually composed of lead sheet. In the case of cadmium, and in fact for most metals, electrowinning is carried out at current efficiencies often exceeding 90%.

4. Molten Salt Bath Electrometallurgy

The most important industrial non-aqueous electrochemical processes are probably the electrowinning of aluminum and magnesium from molten salt baths. In the case of aluminum, a bath of molten cryolite, $NaF \cdot AlF_3$, is used to dissolve a feed of purified alumina, Al_2O_3, which is electrolyzed on carbon electrodes to yield molten aluminum and oxygen. Careful adjustment of voltages and current can eliminate the need for external heating, once the system is in operation at about 1000°C. Ampere efficiency ranges from 85-90%. The oxygen generated at the carbon or graphite anode reacts with it to a significant degree to form CO_2, which, although it diminishes anode life, also helps to generate heat internally and to keep exposing a fresh anode surface.

5. Electroplating

The electroplating industry (including anodizing) is a widespread user of industrial electrochemistry for the preparation of decorative, functional, or protective surface finishes. Literally thousands of plating shops are in existence, some captive to parent manufacturing plants but most independent and small in size (less than 15 employees). Among the metals commercially plated are antimony, arsenic, brass, bronze, cadmium, chromium, copper, gold, indium, iridium, iron, lead, nickel, palladium, platinum, rhodium, ruthenium, silver, tin, zinc, and lead-tin solder alloys. Most plating is from aqueous electrolyte baths with the work piece as cathode and an anode of the metal being plated. During plating, the anode is consumed and maintains the metal ion concentration of the bath at a constant level. Plating may also be done using an inert anode such as carbon at which oxygen is evolved. In such cases, the bath concentration changes with use; generally such baths are prepared at higher metal concentrations than those using consumable anodes. The concentration and composition of plating baths and the current density are generally determined by the type of finish required, the metal being deposited, and the substrate material and geometry. Current efficiency may range from about 10% for some chrome plating to virtually 100% for silver and copper.

B. APPLICATION OF ELECTROLYSIS IN HAZARDOUS WASTE TREATMENT

> "For virtually every type of effluent problem, an electrochemical solution can be envisaged, either by the armchair chemist or his laboratory counterpart.
>
> Electrochemical solutions to problems in effluent treatment are not exempt from those criteria which all processes must satisfy, namely, their cost efficiency as expressed in terms of capital investment costs, and the operation expenses. The would-be practical scientist loses sight of these facts at his peril." (Ref. 2.)

Successful uses of electrolysis in waste treatment may be divided into three broad categories: reduction of a dissolved species at the cathode, such as the plating out of a metal contaminant; oxidation of a dissolved species at the anode, such as the destruction of cyanide; or the useful electrolysis of solvent, as in electroflotation.

Probably the most common application is in the partial removal of concentrated metals from waste streams for recycle or reuse. An excellent example is the electrolytic regeneration of spent copper pickling solutions. In the copper industry, scale and oxide are removed from freshly cast and hot worked copper metal by concentrated sulfuric acid solution. As it is used, the pickling bath becomes loaded with copper, at the expense of its acidity, and loses its effectiveness. It is now fairly routine to employ a small electrolytic cell to plate the excess copper from the solution, simultaneously generating oxygen and hydrogen ions at the anode, and thus maintain the baths at an effective acid concentration. Table 2 shows typical values for such a system in operation.

As the bath is fairly concentrated, operating between 2 and 7% copper, the system is designed much as would be a conventional electroplating bath, the work piece or cathode now consisting of reclaimed and valuable copper.

However, when it is necessary to recover metals from dilute streams, less than about 1%, the rate of removal becomes very dependent upon the rate of diffusion of these metal ions to the cathode surface. Two general approaches have been taken to work around this inherent limitation. One is the vigorous pumping, stirring, and circulation of electrolyte through narrow slits or passageways between electrodes in order to overcome the reliance upon diffusion to supply new metal ions to the cathode. Carefully engineered, this cannot only bring the electrolyte into close contact with the electrodes, but under certain conditions, the metal may be deposited as a non-adherring powder which is washed from the electrode surface and filtered out down stream. Such a system has been reported to operate at 10% cathodic efficiency on a 100 ppm copper stream (Ref. 2).

Similar somewhat to the forced flow system above is one in which electrolyte is pumped through a narrow gap over the surface of a rotating cylindrical cathode. In the case of copper being deposited on a stainless steel cathode, the adherence of the deposited film is minimal and it can be mechanically stripped as a sheet and reused as anode material in

TABLE 2

OPERATING CONDITIONS FOR COPPER RECOVERY CELL

Anodes	PbO_2 (1-2% Ag)
Cathodes	Stainless-steel or copper
Cell temp.	48-65°C
Current density	4-16 mA/cm^2
Cell voltage	2.5-3.5 V
Cu concn. (in)	7%
(out)	2%
Efficiency (C.E.)	70-90 m
Electrode gap	14 cm
Energy expenditure	900 AH-4.5 kWh/kg Cu

Source: Ref. 2

plating. Such systems have been shown to work at low levels of metal, down to about 10 ppm, but again metal reclamation from this bed material can be a problem.

Other cathode reduction processes abound, at least in concept. Most involve the plating out of undesirable metal contaminants, but some do not. For instance, pilot studies have been carried out on the reduction of hexavalent chromium, found in plating wastes, to trivalent chromium which may readily be precipitated out by conventional caustic treatment.

Anodic oxidation schemes generally involve the destruction of specific organic chemicals or the oxidation of cyanide wastes. Cyanide waste destruction in the presence of alkali probably follows the route

$$2CN' \longrightarrow 2CN^{\cdot} + 2e$$

$$2CN^{\cdot} \longrightarrow (CN)_2$$

$$(CN)_2 + 2NaOH \longrightarrow NaCNO + NaCN + H_2O$$

The cyanate then reacts further with excess caustic to yield ammonium hydroxide, ammonium bicarbonate and sodium carbonate. However, all cyanide present, such as that tied up as ferricyanide, may not be amenable to treatment, and thus the process may result in a significant but not complete destruction of cyanide (Refs. 4,6).

In an alternative to this reaction, sodium chloride may be added to the electrolyte, resulting in the production of hypochlorite upon electrolysis. The hypochlorite then reacts with the cyanide to yield ultimately carbon dioxide, nitrogen, and sodium hydroxide. The electrolysis may take place at conventional planar electrodes but more recently fluidized bed electrodes have been found to perform well.

It has also been reported in the literature that waste HCl streams may be at least partially reclaimed by electrolysis to yield usable chlorine gas. However, as the system works only for streams containing in excess of 20-25% HCl, its applications appear quite limited (Ref. 11).

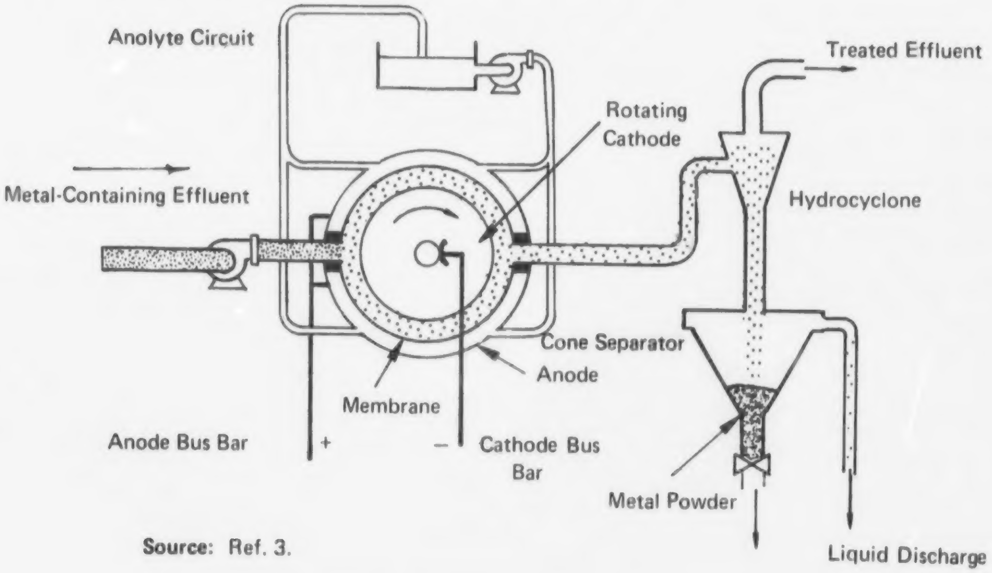
Combining some of the attributes of the two systems mentioned above is a recent development in which a rotating cylindrical cathode is separated from a stationary anode by an ion exchange membrane. As dendritic metal crystals are formed on the cathode, they are stripped away by high liquid flow rates and subsequently removed from the electrolyte. (See Figure 1.) The system is reported to handle metal loads from 100 to 100,000 ppm and to reduce them to levels of 2 to 10 ppm and thus may have application to both recovery and water clean-up.

The second approach is to greatly increase the surface area of the cathode by use of porous materials, woven mats, etc. One such enhanced surface area recently unveiled utilizes a sandwich of mesh anode, plastic screen, and a high surface area cathode rolled into a long spiral cell and inserted into a length of piping. Such a configuration offers high surface area per unit volume, and low resistance to electrolyte flow. It is reported to be effective in reducing metal concentrations below the 1 ppm level, starting with feeds 10-50 ppm (Ref. 10).

Such methods are similar to ion exchange in that the removed material must then be stripped from the electrode or bed for ultimate disposal or reuse. This is not necessarily arduous or impractical but provisions must be made for it. Under ideal conditions the product after stripping is a concentrated metal solution which may be reused elsewhere in the plant or which has other potential credits.

One intriguing method for increasing cathode surface area is the use of a fluidized bed electrode consisting of small spheres of the metal in question or of an inert conductor such as carbon. This technique not only provides for high surface area, but also replenishes the electrolyte at the electrode surface and thus avoids some of the diffusion limitations (Ref. 6).

An extensive program aimed at the use of electrolysis over a fluidized electrode bed to oxidize ferrous ion in acid mine drainage to the ferric state has experienced problems in the deposition of gelatinous ferrous hydroxide at the electrode surfaces with a resultant loss of performance (Ref. 5).



Source: Ref. 3.

FIGURE 1 ELECTROLYSIS SYSTEM

Lastly, electroflotation serves as an interesting example of the indirect use of electrolysis to achieve a useful end in waste treatment. It has been reported widely, and put into practice abroad that electrolytically generated bubbles are used for separation of oil-water mixtures. It is conjectured that this may be due not only to the small size of such bubbles, but also to the presence of some electric charge on the bubbles which affects their interaction with the dispersed oil. Table 3 gives reported data for such a system.

TABLE 3

ELECTROFLOTATION TREATMENT OF STEEL-ROLLING-MILL WASTES

Waste water spec.:	solids (mainly Fe_3O_4)	1500-350 mg/liter
	oils	600-300 mg/liter
	flowrate	75 m^3/h
Treated water spec.:	solids	30 mg/liter
	oils	40 mg/liter

Plant size: $25m^2$ electrode area, $25m^3$ cell volume. Pt-Ti electrodes operating at $100A/m^2$. 8.0 V. Power consumption 275 Wh/m^3.

Source: Ref. 2

Although electrolysis may have some applications in hazardous waste treatment, especially in allowing reclamation of concentrated metal solutions and perhaps scavenging of dilute solutions, it is by no means as straightforward a process as it is often perceived. It is probably significant that the electroplating industry, which would seem ideally suited in terms of both the nature of effluent and skills, has not jumped to adopt electrolysis for waste stream treatment preferring to remain with more conventional chemical treatment methods.

IV. ENERGY, ENVIRONMENTAL CONSIDERATION AND ECONOMICS

A. ENERGY REQUIREMENTS

Electrical energy costs range from 10 to 35% of the total direct operating costs, depending upon the nature of the system. Generally higher costs (lower efficiencies) occur in the treatment of cyanides or very dilute metal streams while direct costs are lower for concentrated metals. Possible trade-offs between energy and capital costs were mentioned in Section A above.

B. ENVIRONMENTAL IMPACTS

Gaseous emissions from electrolysis may frequently be significant, consisting of oxygen, hydrogen, chlorine, and other gases produced either by inefficient reactions at the working electrode or expected reactions at the counter electrode.* Some gases, such as hydrogen and oxygen, may be vented to the atmosphere, provided that certain safety precautions are taken. However, others may have to be scrubbed or otherwise treated.

While it is the goal of most metal deposition schemes to render the process stream disposable or reusable, other systems, such as the destruction of cyanide or the reduction of chromium, simply change the contaminant to a less harmful or more easily treated form; this must then be processed by a separate process. (Nevertheless this should not be reason for eliminating electrolytic processes from consideration out of hand. Use of electrolysis to reduce metal ion concentrations to a sufficiently low level to permit reverse osmosis treatment, or the use of electrolysis to do the final polishing of the product of ion exchange treatment may under the appropriate circumstances result in a viable cost for the total treatment process.)

C. COSTS OF TREATMENT

Waste stream electrolysis is one of that set of processes in which the waste material is removed from the solvent, rather than vice versa. Thus the cost of treatment is very dependent upon the concentration and nature of the undesirable material. For example, even at current efficiencies of 100%, it will take more than three times as much current to remove a ton of copper than a ton of silver, simply because of the great difference in their equivalent weights. However, some examples will serve as useful illustrations of practical costs.

A partical cyanide destruction system based upon the fluidized bed electrolysis of a sodium hypochlorite seeded cyanide stream has been reported to have direct operating costs of about $1.80 per pound of cyanide destroyed. With a feed stream concentration of about

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*The electrode other than the one at which the desired reaction takes place.

110 ppm total cyanide, this is a cost of $1.60 per thousand gallons of water. (But obviously a higher concentration of CN' in the feed would lead to a higher cost per thousand gallons of water.) Capital cost, including pumps and chlorination equipment and cost of installation, were $31,000 for a capacity of 20,000 gpd (Ref. 6).

Costs of metal extraction from dilute streams are equally variable. However, it is reported that a rotating cathode system, such as that produced by Eco-cell, can strip 75,000 gpd of 370 ppm copper at a capital cost of about $15,000. Operating costs are not given, but with a yield of 37 tons per year of reclaimed copper, such as a system would appear cost effective in numerous applications (Ref. 3).

It is worth noting here an interesting and simple trade-off between operating and capital cost which may be unique to electrolysis. Increasing the electrode current will generally permit a greater throughput of feed in a given system (effectively a reduction in capital cost) but at reduced current efficiency (increasing direct costs). Generally systems operating on concentrated solutions favor high current efficiency while systems operating on dilute streams tend to design around lower capital costs, although each situation has to be evaluated in light of all chemical and economic characteristics.

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ELECTROPHORESIS

Prepared by

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I. CONCLUSIONS AND RECOMMENDATIONS

No commercial applications for electrophoresis are known to be in operation at this time. Past uses included creaming of rubber latex, fractionation of hog serum, and concentration of Teflon latex.

It is also used on a laboratory scale for analysis of naturally-occurring mixtures of colloids (e.g., proteins, polysaccharides, nucleic acids).

We do not recommend this process for waste treatment at this time since further commercial application is at least five years in the future.

II. PROCESS PRINCIPLES

Electrophoresis is the transport of electrically charged particles under the influence of a d.c. electric field. The particles may be complex macromolecules* and colloids or particulate matter, either living cells (such as bacteria or erythrocytes) or inert material (such as oil emulsion droplets or clay). Almost any particulate can be made to electrophorese. This report considers electrophoresis for removing electrically charged particles from liquids.

The general principle is based on the migration of charged particles, as a result of the applied d.c. electric field, to a collecting plate for subsequent removal. (See Figure 1.) Because the particles are not allowed to reach the electrode, reactions at the electrode (with the material) do not take place. Particles without charge, isoelectric particles, are not collected. The net result of electrophoretic treatment is thus a reduction of the volume of liquid in which a hazardous material is contained. The membranes which stop the migration of particles are essentially dialyzing membranes (e.g., cellulose) which allow only water and small ions to pass through.

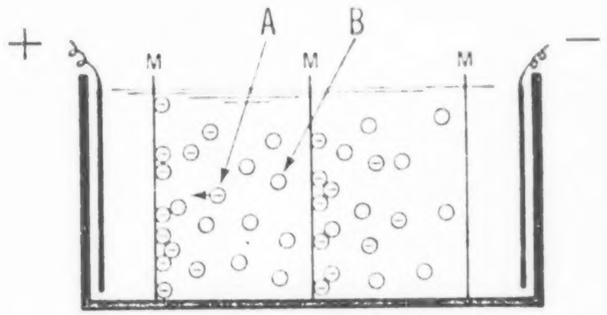

FIGURE 1. BASIC ELECTROPHORETIC REACTOR

Collecting plates M sequester all migrating particles, such as negatively charged particles A, but do not collect the isoelectric particles B.

In order for migration to occur, suspended material must carry an electrical charge, and the liquid phase must carry an opposite charge to preserve electrical neutrality. The source of this apparent charge on the suspended matter is not always evident; it may arise from a partial ionization of one substituent group on a molecule or it may be due to the sorption of ions or ionizable substances on to the suspended material.

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*The transport of simple ions is generally not termed electrophoresis.

Electrodecantation (electrogravitation) is based on the difference in density created by transport depletion of any impurity and the difference in resistivity caused by the transport depletion of ionic species. The first effect causes a film of less dense liquid to rise along the membrane surface on the depleted side and a film of more dense material to fall on the concentrated side. This density difference is amplified by heating effects associated with differences in conductivity of the two films. (The less dense film has a lower conductivity and thus increases in temperature which further decreases its density.) Thus a filtration, which is essentially continuous, is effected by collecting the less dense (purified) liquid at the top of the membranes and the more dense (concentrated) liquid at the bottom of the membranes. (Electrodecantation is sometimes classified as a variation on conventional electrodialysis, rather than a form of electrophoresis.) Electrodecantation was used commercially for a time by Dunlop Rubber Company, for creaming of rubber latex; and DuPont has used the process for the concentration of teflon latex.

Forced-flow electrophoresis is essentially electrophoresis with a superimposed hydraulic pressure. A schematic cross-section of a typical forced-flow electrophoretic cell pack is shown in Figure 2. Another essential change with respect to electrodecantation is the addition of a frictional boundary (F in Figure 2) between the downward flowing colloid-enriched layer and the upward flowing colloid-depleted layer. This filter allows the flow of liquids within the two compartments to be controlled at will by means of pumps thereby avoiding dependence on the uncontrollable element of decantation.

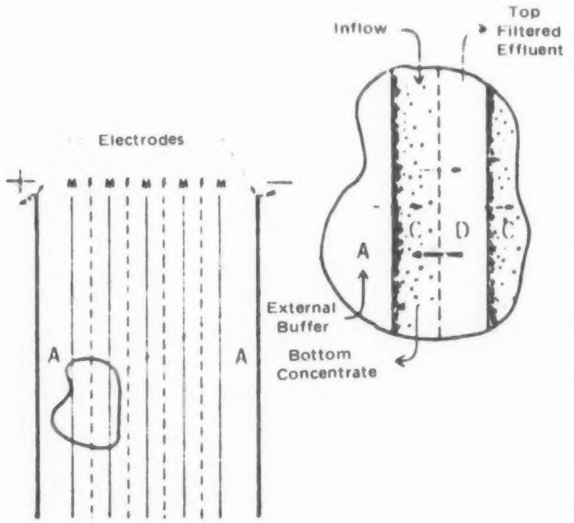


FIGURE 2. SCHEMATIC CROSS-SECTION OF FORCED-FLOW ELECTROPHORETIC CELL-PACK ASSEMBLIES

M and M' are dialyzing membranes, F are filters.

Both aqueous and organic media are suitable for electrophoresis. Aqueous suspensions eliminate the flammability, toxicity, recovery and cost problems encountered in the use of organic solvents; higher concentration solutions and lower voltages may be used, and higher rates of deposition usually result. However, the applied voltage is limited by the possibility of electrolysis of the water at the electrode surfaces, and thus rates may not always be increased by simple voltage manipulations. Presence of even low levels of ionized species such as simple salts may result in these species carrying the bulk of the current rather than the desired "waste." With organic media there are few or no secondary electrode reactions and thus higher voltages may be used to compensate for the lower conductivities.

Electrophoresis may be used to remove quite varied materials from the same codispersion; the differing materials tend to deposit in substantially the same proportion as they are present in the dispersion. In addition, high relative electrophoretic deposition rates (relative to simple electroplating) are possible since the dispersed particles behave as if they have a very large effective ratio of mass to charge compared to simple ions.

Potentially treatable waste forms are:

Aqueous Wastes
Non-aqueous Wastes
Liquids
Slurries (if not too thick)

There is no specificity for different chemical classes with electrophoresis. All that is required is that the suspended (colloidal) matter have a net charge.

The size of the suspended particles that may be removed is in the colloidal range; electrodecantation is said to work best for particles with diameters in the range of one to twenty microns (Ref. 5). Concentrations must be relatively high in order to establish a significant density gradient. Typical feed concentrations for electrodeposition are said to be around five grams per liter; aqueous system voltages are around 15 volts and non-aqueous system voltages from hundreds of volts to over one thousand volts; current densities are about one milliampere per square centimeter of membrane surface (Ref. 5). Flow rates may be in the range of 0.3 to 0.7 liter per square meter of membrane surface, and power requirements around seven kilowatt hours per 1,000 gallons for waste water treatment applications (Ref. 1).

A stack of membrane cells for electrophoretic treatment may be fairly closely spaced, e.g., 0.36 cm for two spacers, a filter and a membrane in one proposed water treatment unit (Ref. 1). This allows a very compact volume for the basic electrophoresis treatment unit, and thus potential application in areas where available space is small.

III. APPLICATIONS TO DATE

While electrophoresis has acquired considerable reputation as an analytical tool, as in the analysis and recovery of naturally-occurring mixtures of colloids (e.g., proteins, lipoproteins, polysaccharides, nucleic acids), no commercial applications are known to be in operation at this time. Only two techniques have so far shown any promise of industrial applications: electrodecantation (or electrogravitation), and forced-flow electrophoresis.

Electrodecantation was used commercially for a time by Dunlop Rubber Company, for creaming of rubber latex; and DuPont has used the process for the concentration of Teflon latex (Ref. 1).

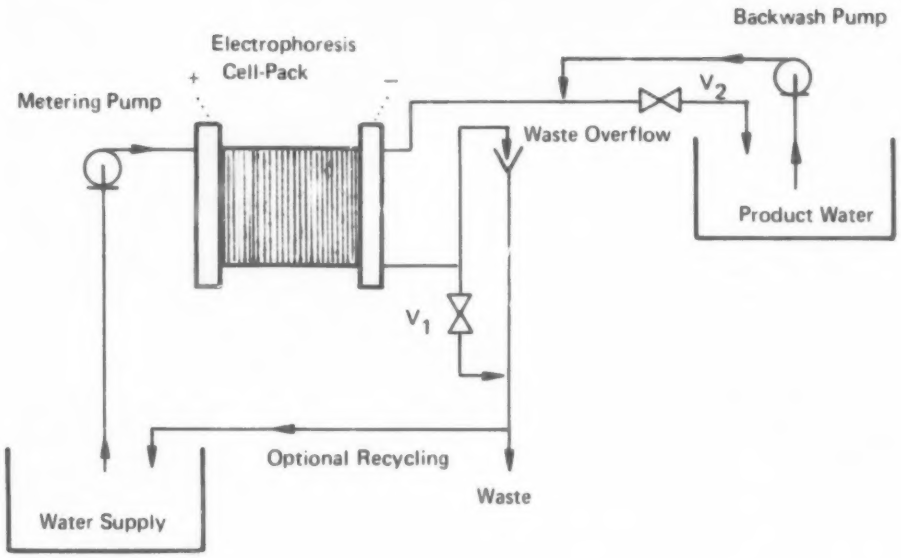
An industrial application of forced-flow electrophoresis to fractionate hog serum, dog serum and other animal sera for veterinary vaccines was undertaken by Anchor Serum (St. Joseph, Missouri) around 1967 (Ref. 2), but was in operation for only a brief period.

Numerous commercial applications of electrophoresis have been proposed (Refs. 1-4) including the following:

- electrophoretic deposition of paints, rubber, and other high-polymers;
- electrophoretic deposition of ceramics, metals and cermets;
- water purification, including reclamation of sewage and industrial wastes, separation of emulsions, color removal, water sterilization (removal of viruses), silt removal, and algae removal.

Laboratory tests have apparently shown that electrophoresis is feasible in these proposed areas of application, including the water purification areas (Ref. 1), but developmental work is not, to our knowledge, being carried out.

Figure 3 depicts a proposed forced-flow electrophoresis (FFE) water treatment plant. The cell pack contains 200 to 400 sq. ft. of filter area, and would occupy a volume of only two to four cubic feet. Note that in spite of the continuous nature of the filtration process, provisions would still be required for the periodic cleaning of the membranes via high velocity backwash, probably coupled with brief periods of voltage reversal.



Source: Ref. 1.

FIGURE 3 SCHEMATIC PRESENTATION OF A PROPOSED FEE PILOT PLANT FOR WATER PURIFICATION

For the production of 10,000 gal./day, 200 to 400 sq. ft. of effective filter area would be necessary.

IV. ENERGY, ENVIRONMENTAL ISSUES AND ECONOMICS

A. ENERGY REQUIREMENTS

Energy requirements may be around 7 kWh/1000 gal for a typical aqueous system. They will be lower when lower conductivity media are used, e.g., low conductivity aqueous solutions or organic solvents. The energy requirements are smaller, per unit weight of material removed, than with processes such as electrodialysis or electroplating. Space requirements are small, resulting in some savings.

B. ENVIRONMENTAL IMPACTS

No serious environmental impacts should be expected with the use of electrophoresis. The concentrated sludge produced must be disposed of if it cannot be recycled, and the "treated" liquid may require additional treatment if hazardous solutes are present. Gas evolution, from electrode reactions, is a possibility.

C. ECONOMIC ANALYSIS

There is no historical basis for estimating the costs of hazardous waste treatment by electrophoresis, because of the paucity of published information and the lack of any recent practical experience on a commercial scale. Capital costs for the electrophoretic cell and associated power supply may be moderate to large in comparison with those of other competing processes. However, capital costs for electrophoresis would probably be considerably lower than costs for comparable electrodialysis cell packs, as the cost of membranes and filters is negligible in comparison to ion exchange membranes (Ref. 1). Operating costs may be on the order of one dollar per thousand gallons with a probable variation of at least a factor of two for differing applications.

A paper published over ten years ago gave the estimated costs for waste water treatment in the range of \$.01 to \$1.08 per thousand gallons. These estimates are shown in Table 1.

Electricity costs based on 7 kWh/1000 gal. and a price of \$0.03/kWh (Ref. 1) would contribute about \$0.21/1000 gal. to the operating costs.

TABLE 1

ESTIMATED (1965) COST ESTIMATE FOR WATER TREATMENT BY ELECTROPHORESIS

Water Sample (1)	Specific Conductance Of		Flow Rate, in Gallons per Hour per Square Foot (4)	Power, in Kilowatt Hours per Thousand Gallons (5)	Estimated Cost, in Dollars per Thousand Gallons	
	Raw Water, in Micromhos per Centimeter (2)	Finished Product, in Micromhos per Centimeter (3)			Model (6)	Scale-Up (7)
Silt Separation (flood runoff)	250	67	1.9	62	1.24	0.41
Algae Separation (sewage effluent)	1,100	450	2.6	162	3.24	1.08
Color Removal	64	15	0.4	12	0.24	0.08
(Kitt Peak)			3.7[a]	1.2	0.03	0.01

[a] 83.3% color removal.

Source: Ref. 1.

V. OUTLOOK FOR INDUSTRIAL WASTE TREATMENT

Theoretically, the electrophoretic treatment of hazardous wastes is possible. The problem is that no suitable equipment is available; to the best of our knowledge, none is being developed.

Development of practical applications is not expected to be straightforward because there are several critical aspects of equipment design including:

- electrode reactions — which may have to be suppressed or circumvented;
- pH — adjustments may be necessary;
- conductivity — which may have to be below 300 micromhos/cm in aqueous systems;[1]
- flow — to avoid turbulent mixing in the cells;
- temperature; and
- factors affecting membrane plugging, including backwash techniques — the most serious problem.

Even with proper control of these variables there is no assurance that high removal efficiencies can be obtained at acceptable flow rates without careful piloting of the proposed system.

With federal support, some waste treatment applications could conceivably be developed in five years. This would allow time for two to three years of laboratory development and two to three years of pilot scale development. In view of the minimum level of activity in this field at present, and the lack of scientific and practical guides available, a more realistic time frame for development is five to ten years or longer.

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